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LIGHT AND ELECTRIFICATION.

IF an ordinary gold-leaf electroscope with a freshly scraped zinc cap or knob is charged with negative electricity, and is then exposed to the unfiltered rays of a source of ultra-violet light, its charge will leak away rapidly.

If, further, the electroscope so treated be extremely sensitive, it will be found not only to lose its negative charge, but to acquire a slight trace of positive charge under the action of light.

These are the simple and fundamental facts of what is virtually a new subject or branch of physics, the subject of photo-electric action, the influence of illumination on electrified surfaces.

SUMMARY HISTORICAL SKETCH.

The above facts were discovered by Hallwachs, but their discovery originated in an observation made by Hertz, that the sparking of an induction coil was facilitated when the light of another spark fell upon its secondary terminal. Hertz proved conclusively that this was a real action of light, and not due to some more direct electric action, nor yet to any convection of chemical or dissociated products from one spark to the other, such as Schuster and others have found to be likewise a real and genuine effect having influence on some forms of electric discharge. Hertz also tried other sources of light, and by passing the rays through

a quartz prism established the fact that it was the ultra-violet rays which were specially active. In fact if a thin sheet of glass were interposed, so as to cut off the extreme and invisible ultra-violet rays, the action ceased; though a layer of water was transparent to the action, except when certain salts were dissolved in it; while coal gas was remarkably opaque, and stopped the action when interposed in a sufficient stratum between the two sparks. He further modified the experiment by taking the sparks between different metals in different gases, and in air at different pressures. He thus found that in rarefied air the effect was exaggerated, and that an atmosphere of hydrogen was rather better than one of air. He also found that the region of the spark terminals near the negative pole or cathode was the most sensitive part of a spark gap, so that, in fact, the main photo-electric influence depended on whether the region near the cathode surface was or was not illuminated.

The subject was taken up by a number of experimenters, among whom Wiedemann and Ebert specially examined the effect in different gases, and established the fact that the illumination operated only on the cathode surface or negative pole, and that illumination of the anode, or of the air between the terminals, had little or no influence on the discharge. Supplementing this, Hallwachs, and later Hoor, discovered that a freshly cleaned metallic surface lost a negative charge quickly under the action of light, but retained a positive charge; while Hallwachs and Righi independently and simultaneously discovered that such a freshly cleaned metallic surface, when exposed to light, not only discharged any negative electricity it might possess but was able actually to acquire a slight positive charge. Lenard and Wolf also made the important observation that a negatively charged or an uncharged metal seemed to evaporate, or throw off something which might be called "dust," under the action of light. Other investigators into the subject who must be mentioned are Stoletow and Branly, but probably none have worked at it more energetically and successfully than the well-known coadjutors of Wolfenbüttel, Messrs. Elster and Geitel, who have dis-

covered many remarkable facts in connection with it. It was not till the beginning of 1894 that the subject was seriously taken up by the writer.

This brief outline of some of the work that has been done in this subject since its discovery in 1887 must serve instead of a proper historical sketch, because we want to pass from the consideration of the investigators to a study of the facts themselves.

EXPERIMENTAL DETAILS.

A demonstration of the fundamental fact can be made with very simple appliances, but unless they are properly arranged it is easy to fail. Several experimenters have indeed doubted the fact because they were unable to repeat it. No method can be simpler than the one indicated in the first few lines of this article; and with a well-insulated electroscope, whose rate of leakage can be timed, the only difficulty is the obtaining of a suitable light. Sunlight on a mountain top is certainly effective, but sunlight on a plain is much weaker, and in a British town (perhaps even in the British Isles) it has hardly any power at all; the active rays are all filtered out by the gross and polluted atmosphere usually existing above such places. Visible brightness of illumination is not what is wanted, the most effective rays are invisible; for instance, Hertz observed that the oxyhydrogen flame was just as effective before the lime was introduced into it as after, and that it is the bottom blue part of a candle flame which possesses any power at all; hence the light from a brush discharge or from the aureole surrounding an induction coil spark is very much more effective than, for instance, the lime light or even the magnesium light. An arc-light is, however, the most powerfully active source, especially if it is made extra long, and still more if a little zinc is placed in the positive crater for volatilisation. Hertz himself noticed that the violet flame between the poles was more active than the intensely bright carbons themselves. In using the arc-lamp it must be understood that is to be naked. There are to be no lenses in the lantern, or if there are,

they must be composed of quartz or other really transparent substance.

The statements here made about the need for extremely ultra-violet rays are, however, subject to modification with the nature of the gas surrounding the metallic surface, for Wiedemann and Ebert found that in an atmosphere of carbonic acid even visible rays produced some effect; and a still more marked modification is dependent on the nature of the metallic surface. I have spoken of zinc as a suitable metal, and so it is; but, with highly ultra-violet light, copper, silver, and even platinum, do nearly as well. With light of lower refrangibility, zinc is better than the less oxidisable metals, but, as Elster and Geitel have found, potassium or sodium is better still. With such metals indeed any kind of light serves, not only ordinary diffuse daylight, but even the light of a candle.

INFLUENCE OF THE KIND OF METAL.

It appears that the order of metals in photo-electric power, when tested by their discharging action for negative electricity, is the same as their order in the voltaic series, the alkali metals heading the list, and the noble metals being the least effective. With light of ordinary wave lengths, indeed, such as come easily through glass, only the alkaline metals, or those above zinc in the voltaic series, have any real power; but with short enough wave lengths all metals are competent to show the effect, though the noble metals require light of an extremely high ultra-violet character.

This fact of the voltaic order of the metals clearly suggests some chemical or semi-chemical explanation, but it may be well to defer coming to a conclusion on that point for the present.

DISCHARGING ACTION OF METALS FOR POSITIVE ELECTRICITY.

Hitherto we have spoken, as the earlier experimenters in the subject did, as if negative electricity alone was discharged while positive electricity was retained.

If the surfaces are very clean, and if the light is ordinary ultra-violet light, the difference between the rates of discharge of negative and positive electrification is so enormous that it is practically true to say that one pours away while the other is retained; but more careful observation will show that the rate of leakage of positive, too, is usually increased by illumination. The leakage of positive, however, occurs better from surfaces not too recently cleaned, and it appears as if still shorter wave lengths were necessary for it than for leakage of negative.

My experiments go to show that as metals get dirty the rates of leakage of negative and positive become more comparable. And one metal I have found which is able to discharge positive even faster than negative, *viz.*, cobalt. What the meaning of this exceptional behaviour may be is quite unknown, but the general rule seems to be that the discharging order of the metals follow the voltaic series, and that the more oxidisable metals discharge negative more easily, and under longer wave lengths, than do the less oxidisable. Righi further finds that the tendency of metals to become positively charged under the action of light likewise follows the voltaic order, but inversely; gold and carbon being more effective in acquiring a positive charge than zinc and aluminium. It may be doubted whether this is capable of thorough substantiation as a general law or not, but there can be no doubt that the discharge of negative electricity is most rapid from perfectly clean metals;—they need not be polished, scratching with sandpaper suffices, but a few minutes' exposure to air destroys the initial extreme vigour of the effect. It is not true that a positive charge is wholly retained under the action of light even by such clean metals; they do discharge it, but very much more slowly than they do a negative charge; whereas when they are tarnished the rate of discharge for the two kinds of electrification is more nearly equal, and when they are dusty or dirty it is quite possible for positive electricity to be discharged more rapidly than negative by the action of light. The following extracts from my laboratory note-book may serve to establish and illustrate this fact:—

Platinum plate dirty with age connected to a measuring electroscope and illuminated by an arc-lamp, showed a definite fall of potential when charged negatively, passing from mark to mark on the scale in 120 seconds; when charged positively it showed the same fall of potential in 100 seconds. Platinum plate scratched clean with glass-cloth, and similarly treated, showed the same amount of leak in $6\frac{1}{2}$ seconds when negatively charged, but when positively charged it still took 100 seconds.

Here is another example. A clean zinc plate, the same size as the above platinum, leaked at exactly the same rate in the strong rays of an arc-lamp, *viz.*, negative in $6\frac{1}{2}$ seconds, positive in 100 seconds; but, when a dirty piece of zinc was employed, the time required for the same amount of leak was 30 seconds for negative and 65 for positive.

Most clean metals on this occasion gave about the same rate of leak, but tin plate seemed rather exceptionally quick. Its rate for negative was 4 seconds, and for positive 80 seconds.

THE QUESTION OF FATIGUE.

Lapse of time makes any metallic surface less powerfully photo-electric, simply by reason of tarnishing or accumulation of dust; but the question arises whether light itself has any effect in accelerating this decay of the power. To try this a couple of similar plates have been kept for some hours, one in the blaze of the arc, the other in comparative darkness, and then their rates of leak compared. The only metal which showed a distinct effect of this kind was palladium. Palladium appears to get rapidly fatigued by the action of light, so much so that its fatigue is noticeable in a simple series of leakage experiments taken one after the other.

Another experiment, something of the same sort, was to reflect light down on to the surface being tested, by a clean silver-on-glass mirror. The mirror could be kept charged either negatively or positively, and, of course, under these conditions it itself discharged rapidly, especially when negative; but the question was whether light thus reflected

from a discharging mirror had become at all inactive, or whether it was still equally competent to exert a discharging action on any second surface which it met. The latter seems to be the truth; whatever fatigue may be experienced by a *surface* none seems experienced by a *light;* or if the light was affected, there was too great a balance of power left to make its deterioration of quality conspicuous. It is, however, an important question whether the short waves which are especially operative are really consumed in the act of effecting the electric discharge, or whether they are uninjured; and hence the experiment was carefully and repeatedly performed. No question of energy arises, because the energy of the discharge may be simply and entirely electrical.

NON-METALLIC SUBSTANCES.

Elster and Geitel found that luminous paint was peculiarly active as a discharging agent, and they tried other phosphorescent bodies too, also several minerals. In my experience some minerals discharge positive more readily than negative, but any surface to be effective should be dry. A lump of dry soft red sandstone fell in potential a given amount in 150 seconds when charged positively, whereas when charged negatively it fell much more slowly or not at all. On the other hand many non-metallic bodies imitate metals in their more rapid loss of negative electricity. Thus a piece of gas-carbon lost negative in 18 seconds, positive in 150; lamp-black lost negative in 10 seconds, positive in 120.

PLANTS.

Several growing plants, and cuttings of others, were tried in my laboratory last June, with the result that several of them discharged positive more readily than negative; but on the whole the rates of discharge for the two kinds of electrification from the leaves of plants under the action of light are more nearly equal than are the rates of discharge from most other substances. Some facts suggest that the time of year, *i.e.*, the state of the plant, has an

influence ; and we conjecture at present, as the result of observation, that in summer when the leaves are fresh positive electricity is most easily discharged, whereas in late autumn negative seems to gain the advantage. A geranium in a pot was the first thing tried (in June), and it then discharged positive five times as quickly as negative. In all cases it must be understood that the action is due to the ultra-violet rays: glass cuts off the effect, quartz transmits it.

Garden soil was also tried, and when dry it has a very fair discharging power, usually rather quicker for positive than for negative.

TENSION OR POTENTIAL.

In a future article we may endeavour to discuss the physical aspect of some of these facts from the point of view of theory, but it is plain, in the experiments on metals at any rate, how clearly a quasi-chemical origin is indicated for the discharging power. That being so, it is essential to ascertain whether the effect depends on the potential of the electrified metal, or whether it is dependent on surface density. It is easy to have a metallic surface at a high potential without a trace of electric charge: such is the inside of a metallic enclosure, or practically of any highly charged hollow vessel; its surface density and its electric tension will be nothing, though its potential may be thousands of volts. Conversely, it is easy to have a surface charged to a high density and with an electric tension at the point of bursting, while yet its potential shall be zero. This is the case of an earth-connected surface exposed to the inductive influence of a highly charged insulated body.

It is a simple question for experiment to decide whether the discharging power of light operates in one of these cases and not in the other. Or, briefly, does the discharging power of light on a surface depend on the tension or on the potential of that surface?

The answer is distinct; it depends upon tension. If the surface is not actually charged with electricity, light has no effect; or at least its effect is limited to the feeble

charging with positive which so many experimenters have observed, and which we may assume at present to be correct; though whether it is a true and simple effect we will not at present consider quite decided.

The inside of a metallic vessel is not affected by light, even when the air contents are blown out and exchanged for fresh air. Unless the atmosphere is thus changed the experiment is inconclusive, because, even if a charge were to leave the interior surface of the vessel and pass to the air in contact with it, an electroscope connected to the vessel would of course show nothing; the charge must be extracted entirely from the vessel before its potential is affected. However, if proper precautions are taken about blowing in non-electrified air (by no means an easy matter), the experiment is perfectly negative; no discharging action occurs from a surface at zero density.

If the beam of light which has been shining on the interior of a charged pewter pot is transfered and made to impinge on an outer edge of the same vessel the leak of electricity immediately becomes rapid.

On the other hand, a surface connected to the earth (and therefore at zero potential) pours away its induced charge rapidly when a beam of suitable light falls upon it. And, indeed, this is a favourite and easy mode of testing the power of different substances; *viz.*, by exposing them to the inductive influence of a charged body, such as a layer of wire gauze, through which light has easy access, and observing the rate of leak either by the rise in potential of an electroscope attached to them and initially at zero, or by a very sensitive galvanometer inserted in the circuit which connects them to earth. Indeed, with a water battery or other source of high EMF, nothing further is needed than a sensitive galvanometer and the two surfaces facing each other across a narrow air space, which under the action of light becomes virtually conducting.

EFFECT OF MAGNETISM.

One of the most singular observations on the subject was made by Elster and Geitel, who placed the poles of a

magnet in various aspects with respect to the line of discharge or of conduction between two plates in vacuo, such as are mentioned just above.

They found that if the lines of magnetic force agreed in direction with the lines of electrostatic force they had no appreciable influence on the discharging power of light; but that as soon as the magnetic and the electrostatic lines crossed, the discharging power of light was definitely diminished and interfered with.

QUESTION OF INTENSITY OR TOTALITY OF ILLUMINATION.

Experiments made in my laboratory were directed to ascertain whether the action of light depended on its concentration or on its total amount. To this end a large metal plate was set at different distances from the source, in a cone of rays, so that at one time a very small area, and at another time a larger area, was exposed to the same total quantity of light.

No very minutely accurate measurement was possible, because an arc-light is subject to capricious variations,—the long fizzing arc being much the most effective; but certainly if there is any effect due to concentration it is very small. On the average the rate of leak was just the same when the light was spread over a large area as over a small.

INFLUENCE OF THE DIRECTION OF THE LUMINOUS VIBRATION.

Another vital discovery was made by the Wolfenbüttel experimenters, by aid of their beautiful method of employing the alkali metals for the purpose in partial vacua in glass bulbs. The alkali metals are generally superior to others by reason of the fact that ordinary visible light is powerfully effective in their case, so that glass is no deterrent, and candles or diffuse daylight may be used. This is convenient for measuring purposes, because of their great steadiness as compared with an arc; and another convenience is the possibility of using a liquid metallic surface, *viz.*, that of the liquid potassium-sodium alloy. Mercury is comparatively inert, but a liquid surface has the great merit

of being perfectly smooth and horizontal; it thus makes easy definite optical experiments on angles of incidence and azimuth of polarisation. Employing the potassium-sodium alloy in a hydrogen-vacuum, Elster and Geitel found that the most effective light is that which is polarised perpendicularly to the plane of incidence, *i.e.*, light whose vibrations have a component normal to the surface. Light vibrations parallel to the surface are comparatively inoperative.

If this be so, of course it follows that with common light normal incidence should be less effective than oblique incidence; and indeed it may be supposed that any effect of normally incident rays might largely be due to the scratched and unpolished state of ordinary metallic surfaces. Experiments conducted in my laboratory on polished surfaces of silver do not bear this out. Normally incident light has a very considerable effect, at least on ordinary surfaces in air, though obliquely incident light has a greater. Using the liquid K—Na alloy it was possible to verify completely Elster and Geitel's result with respect to the azimuth of polarisation, and we also found that with common light and different angles of incidence the effect increased rapidly as the incidence changed from normal (0°) to something near 60°, but that it then ceased to increase any more. So far as I have observed, the effect of polarisation and varying incidence is much more marked with these alkaline metals in vacuum, subjected to long waves, than it is with such surfaces as polished zinc or silver in ordinary air and other gases, exposed to ultra-violet waves; though with these also it is perfectly real and definite.

I have now rehearsed what may be considered as a summary of most of the more prominent and interesting facts connected with the subject, abstaining from any theoretical comment. In a future article the attempt may be made to collate these facts, and to consider their bearing with reference to a possible explanation or perception of the meaning of the effect, so far as it is reasonable to suppose it understood at present.

OLIVER J. LODGE.

TWO FUNDAMENTAL "LAWS" OF NERVE-ACTION IN RELATION TO THE MODERN NERVE-CELL.

IT would be difficult to point to any recent series of investigations more widely known than those on the minute anatomy of the nervous system, or to name any one investigator whose publications have had a more widespread effect upon current literature than those of Ramon y Cajal.

Histologists, physiologists and neurologists have concurred to testify to the importance of these investigations, and to the light thrown by them upon the anatomy, physiology and pathology of the central nervous system.

There can be no doubt in the mind of any one who has had the opportunity of examining Cajal's preparations, that the silver method has enabled us to see further along the ramifying processes of nerve-cells, and that our knowledge *de visu* of their minute anatomy is thereby extended. And in so far as an extension of the anatomical basis is of necessity an added support to our physiological and pathological conceptions, physiologists and pathologists may fitly recognise their indebtedness to the silver method, and to Professor Cajal in particular, who has prosecuted it with conspicuous zeal and success.

It is possible, however, that we may be led astray in our appreciations, and by becoming satisfied with the vague statement that a great light has been cast upon the physiology of the nervous system, omit to recognise the actualities and possibilities shown up by that great light.

For the last four or five years I have found it necessary, in lecturing on the physiology of the nervous system, to allude to the results of the silver method. Until two years ago I was forced to limit myself to the descriptive histology of the bushes and baskets and collaterals, without venturing to append to such description any physiological remarks whatever as to their possible functional significance *qua*

direction and propagation of nervous impulses. The cell of Golgi and Cajal bore no functional interpretation other or more precise than was already placed upon the cell of Deiters; in either case the distinction between nervous and protoplasmic processes appeared to be equally gratuitous; and as regards the formation of elementary notions, the collateral branches of axis-cylinder processes and the discontinuity of fibrous network and nerve-cell, however significant these facts might some day prove to be in relation to the transmission and diffusion of nerve-impulses, were for the moment obstructive rather than auxiliary.

The anatomical descriptions of collaterals were obviously selected under the guiding influence of physiological considerations. Those of pericellular networks simply signified to us that continuity of structure was not indispensable to propagation of nerve-impulses. Collaterals were pointed to as the distinct continuous paths by whose presence we might understand the manifold radiations of nerve-impulses. On the other hand, arborisations of fibrils, their want of protoplasmic continuity with cells and with each other, instructed us to regard continuity of protoplasm as an unessential condition of nerve conduction.

Therefore it was that while introducing into lectures such knowledge as I possessed concerning the then newer histological developments associated with the names of Golgi, Cajal, Retzius, I deliberately omitted from a written introduction to physiology any detailed description of anatomical facts to which no plausible functional significance could be reasonably assigned. The omission of such well-known and important facts was criticised by more than one of my friends, without, however, adding to my knowledge more than that it was inexpedient to omit mention of such remarkable researches.

I held, and hold, that it is inexpedient to prematurely introduce into elementary teaching the latest "discovery" in physiology and *a fortiori* in histology. Yet so far from ignoring these particular researches, they had been an object of my frequent consideration and speculation. And that to such an extent that the speculation took precise

shape in the diagram and table that I now submit to criticism, and which has served me as a lecture text for the last two years to my more advanced students. I may emphasise here, as I have done *viva voce*, that the diagram embodies a mere speculation, but a speculation that, even if false, binds together under one generalising bracket three dicta, two of which are now universally admitted to signify correct data, while the third, although more recent, is also allowed to rank among admitted data. These are :—

(1) A nerve-cell has a trophic influence upon a nerve-fibre.

(2) Nervous impulses pass round the nervous system in one direction only.

(3) A nerve-cell is in protoplasmic continuity with a nerve-fibre by one pole only.

The dependence of (1) and (2), which are statements of well-assured physiological fact, upon (3), which is a statement of less well-assured anatomical fact, will be at once brought clearly before the mind by referring to the case in which they most obviously apply, *viz.*, the anterior cornual cells and their relations to pyramidal and motor fibres. These relations can be most easily exhibited in the following diagram :—

A pyramidal fibre *py* terminates in a pericellular feltwork of fibrils, and is not in protoplasmic continuity with an anterior cornual cell.

A motor fibre *m* is in protoplasmic continuity with an anterior cornual cell.

After a section at 1, degeneration occurs below the point of section as far as but not beyond the cornual cell; there is no degeneration above.

After a section at 2, degeneration occurs below the point of section, and not above.

Nervous impulses can be transmitted in a downward direction through the cell from *py* to *m*, but cannot be transmitted in an upward direction from *m* to *py*.[1]

[1] Gotch and Horsley find—or more correctly speaking infer - that the anterior cornual cells block centrifugal impulses partially, and centripetal impulses completely, but strangely enough neglect the best and best-

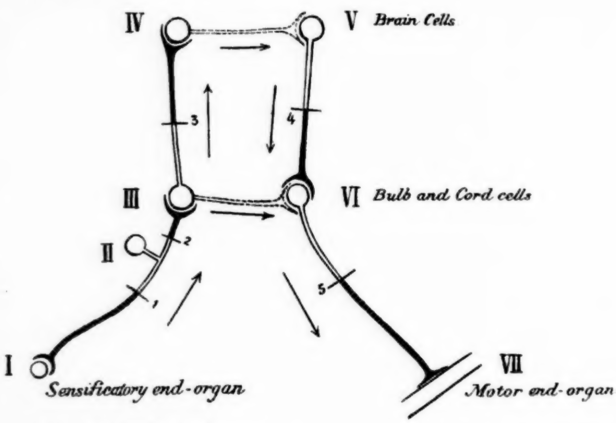
These several facts form a group of ideas in which the connecting consideration may be brought out and expressed by saying that, by virtue of the anatomical interruption of continuity, the anterior cornual cell plays the part of a nerve-valve—permitting the passage of nerve-impulses in a centrifugal direction, obstructing them in a centripetal direction—and that the interruption is a determining factor as regards Wallerian degeneration of nerve-fibres. Degeneration occurring below 1 and 2 is in no known relation with the fact that their tract is efferent,[1] but is in accordance with the fact that the part below *py* is not in protoplasmic continuity with any cell, while the part below *m* is in protoplasmic continuity with an anterior cornual cell ("trophic"). We may understand better from this point

known grounds upon which the same conclusion had been based, and place it upon the extremely insecure basis of their own electrical experiments, presenting it as a surprising discovery, and linking it in a curiously confused way with psychological theories concerning kinæsthesis. They find, moreover, or infer, that centrifugal as well as centripetal impulses can pass down the posterior roots, and apply this "fact" in a similar manner to support their views of kinæsthesis (Gotch and Horsley, *Phil. Trans. R. S.*, 1891. *Croonian Lecture*, p. 509). For a criticism of these views see Waller, "On the Functional Attributes of the Cerebral Cortex," *Brain*, p. 384, 1892.

[1] The misconceptions still prevailing as to the fundamental facts of degeneration, as expressed in recent and authoritative text-books of Anatomy and of Physiology, are survivals or sports that are very difficult to account for. "The pathological method depends upon the trophic influence exercised by nerve-cells. It is found that every nerve-fibre must receive a certain influence from a nerve-cell in order to benefit by the lymph with which it is surrounded. This is called trophic influence. The trophic cells for the sensory fibres are situated in the ganglia in the posterior roots; hence if the roots be divided between the cord and the ganglia, the nerve-tracts degenerate in an upward direction, and the degenerated tracts can be seen surrounded by the unaffected tracts. *Ascending degeneration is therefore characteristic of centripetal tracts*" (Morris' *Anatomy*, 1893). This being precisely what is *not* the case. When a nerve trunk is cut across, the degeneration actually descends, in the sense that the progress of the degenerative changes may be traced downwards; they begin at the section and travel downwards at a rate sufficiently slow to permit a difference being observed between the progress of degeneration at a spot near the section and that at one farther off (Foster's *Physiology*, 5th ed., 1890, p. 871). Which is a very graphic description of what does *not* occur.

of view how section 1 across a fibre *py* causes degeneration below but not above, than upon the older view that the fibre *py* is in continuity at both ends with a cerebral and a spinal nerve-cell.

But the full possible significance of the nerve-valve conception as regards direction of Wallerian degeneration and direction of nerve-impulses comes out better on examination of the following diagram and table, which, besides this best-known case of the efferent tract, gives all the less well-known cases that present themselves in the afferent tract as well :—



I. Sensificatory end-organ.
II. Ganglion cell of posterior root.
III. Spinal cell of Clarke's column, and of Burdach's bulbar nuclei.
IV. "Sensory" brain cell, cerebral and cerebellar.
V. "Motor" brain cell.
VI. Spinal cell, bulbar nuclei and anterior cornu.
I. III. IV. afferent tract. V. VI. VII. efferent tract.
From I. to III. periphery to medulla ; afferent nerve-fibres.
From III. to IV. medulla to cortex; Goll's column; cerebellar tracts; crura cerebri.
From V. to VI. cortex to medulla; pyramidal tracts.
From VI. to VII. medulla to periphery; efferent nerve-fibres.
III. to IV. spinal communication.
IV. to V. cerebral communication.

Impulses can pass from I. to III., III to IV., V. to VI., VI. to VII., also from III. to VI., IV to V.

Impulses cannot pass from VII. to VI., VI. to V., IV. to III., III. to I., nor from VI. to III., V. to IV.

The above schema of the physiological anatomy of the nervous circuit is intended to embody the best attested facts

Section.	Channel.	Above Section.	Below Section.
At (1)	Afferent fibres of posterior root.	No degeneration; continuity of fibres with ganglion cells of posterior root.	Degeneration, reaching to periphery.
At (2)	Afferent fibres of posterior root and of Goll's column.	Degeneration, reaching to spinal grey matter (Clarke's column, Burdach's nucleus).	No degeneration; continuity of fibres with ganglion cells of posterior root.
At (3)	Afferent fibres of the cerebellar tract.	Degeneration, reaching to cerebellum.	No degeneration; continuity of fibres with cells of Clarke's column.
At (4)	Efferent fibres of the pyramidal tract.	No degeneration; continuity of fibres with cells of Rolandic area.	Degeneration, reaching to cells of anterior cornua.
At (5)	Efferent fibres of anterior root.	No degeneration; continuity of fibres with cells of anterior cornua.	Degeneration, reaching to periphery.

regarding the trophic and functional relations of its principal cells and cell-connections, and to illustrate (*a*) the *law of trophic action*, (*b*) the *law of forward direction*, in conformity with modern histological views.

The *law of trophic action* is to the effect that the nutrition of nerve-fibres is dependent upon their protoplasmic connection with nerve-cells, and is established upon the following data.

Sections 1, 2, 3, 4, 5 produced effects, the situation and extent of which are indicated by the blackened tracts.

The *law of forward direction* is to the effect that functional impulses pass in the direction of the arrows from I. to VII., and in that direction only.

No attempt has been made to represent "collateral" connections. Communication between III. and VI., and between IV. and V., the existence of which we are forced to infer from physiological consideration, is indicated by dotted lines.

The cells and pericellular networks pointed out by

modern histologists are indicated by black circles and surrounding semicircles, and it is to be noticed how by their disposition the figure gives expression to a common hypothesis embracing the facts of Wallerian degeneration, and the probability of the law of forward direction in the nerve circuit in so far as it may conceivably depend upon a valve action of cells and pericellular network. The data that render that law highly probable are the well-known facts that excitation of the central end of an afferent nerve, and of the peripheral end of an efferent nerve, provokes movement, while that of the peripheral end of a pure afferent nerve, or of the central end of a pure efferent nerve, produces no effect.

I have alluded to the law of forward direction as being "highly probable" only, inasmuch as there are experimental data on record contradictory of that law, which cannot therefore properly be presented as an undisputed statement. Gotch and Horsley, while confirming the fact that impulses up the efferent root cannot act retropulsively, conclude that efferent or retropulsive impulses can pass down afferent channels. Wundt again accepts the possibility of retropulsive discharge along afferent tracts by admitting that a hallucinatory disturbance of the brain may be propagated down the optic nerve to the retina. Nevertheless, on a balance of probabilities, I am tempted to agree with James, who regards the law as an indubitable truth rather than as an hypothesis. [1]

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A. D. WALLER.

[1] And Schäfer, in his recent presidential address to the Neurological Society, arrives at the same conclusion, *viz.*, "that the ordinary centrifugal paths are blocked for centripetal impulses, although the centripetal paths may convey centrifugal impulses, this physiological difference being correlated with a difference of anatomical relationship at the junction of the respective nerve-elements".

ON THE ANTITOXINS OF DIPHTHERIA.

AT the present time there can be no question as to the nature and value of the connection between the biological sciences and applied medicine. Experimental science, which in its infancy advanced along lines widely separated from medicine, has now become closely associated with this, and to an extent impossible for any one to have predicted a quarter of a century ago. This is especially evident in considering the present state of preventive medicine, which is often erroneously held to have been developed by purely legislative measures, while the extensive researches carried out in the laboratory that have really created the subject are often altogether ignored. Inquiries into the exciting causes of infective diseases can be carried out by methodical investigations in a given district, or by experimental researches, and the latter, beyond doubt, has proved a more fruitful source of knowledge, since the abundant evidence that many diseases are directly caused by bacteria has been acquired by laboratory work.

A study of the etiology or causes of disease must of necessity bring the inquirer face to face with a problem which is as old as the history of medicine itself. It is a matter of common observation that certain diseases attack certain individuals, and leave others unharmed. The expression of this in its widest sense is found in the conceptions of susceptibility and immunity. If the latter state is transferable from one organism to another, then it is obvious that the former may be entirely abolished, and a measure of this nature may be termed prophylactic. If, on the other hand, a disease already developed is arrested in its progress by a similar experiment, then a directly curative principle is involved. The future of preventive medicine, at any rate from the bacteriological view, lies in solving the problem of immunity, and this has now entered upon a stage of great interest. Among infective diseases diphtheria has recently attracted considerable attention, since

notwithstanding a steady improvement in general hygienic conditions this disease has steadily increased, especially in towns where formerly it was of rare occurrence, and in addition to this undoubted fact the daily press, both in this country and abroad, has during the last few months described with more or less accuracy the details of a new treatment for diphtheria which has been extensively practised on the continent, and is now upon its trial in this country.

Diphtheria is allowed by every one to be a contagious disease, and the precise diagnosis of this can only be effected by bacteriological examination. In this way it is possible to differentiate various conditions of the throat which may simulate genuine diphtheria, a malady always associated with and dependent upon the presence of a bacillus first observed by Klebs (1), and independently studied and cultivated by Löffler (2) in 1883. This observer isolated two schizomycetes, a streptococcus and a bacillus, from diphtheritic membrane. "The latter has the same length as the bacillus tuberculosis, and about double the thickness. The larger rods are composed of separate links, and where the joints occur a knot-like thickening is often seen. In a not inconsiderable number of individuals a terminal swelling is observed, and sometimes this is found at both ends." The bacillus can easily be cultivated as a saprophyte upon various solid and liquid media. It grows with varying degrees of vigour in bouillon or milk, in urine (3) or Ouchinsky's medium (4); on coagulated white of egg, or potato slabs made alkaline, and upon gelatine, glycerine-agar, solid blood serum, or a mixture of this with bouillon. The latter, known as Löffler's blood serum, consists of a mixture of three parts of serum from the ox and sheep added to one part of beef bouillon, and this medium is claimed to be as admirably adapted for the growth of bacillus diphtheriæ as Pasteur's fluid is for yeast, or Raulin's fluid for aspergillus niger. Löffler (5) himself states that colonies can be recognised four hours after streaking (and Hesse (6) says earlier than the third hour), since the growth of this micro-organism has

outstripped that of any other bacteria originally associated with it. Practically this is by no means always the case, since a large percentage of cultures at the end of twenty-four hours show vigorous growths of streptococci and allied pyogenic cocci. Deycke (7) has given the following formula for a culture medium which is claimed to be even more sensitive than that of Löffler. 1 per cent. solid alkali-albumin prepared by Merck of Darmstadt, ·5 per cent. sodium chloride, 2 per cent. agar, and 5 per cent. glycerine. This is neutralised and then made alkaline by the addition of 1 per cent. soda solution containing 1 part of soda to 2 of water. With this medium Wolff (8) has isolated diphtheria bacilli from the cavities of the tympanum, frontal sinuses and antrum of upper jaw. When inoculated into guinea pigs the bacillus gives rise to a diphtheritic process which may be followed by temporary paralytic symptoms similar to those pathognomonic of human diphtheria. This micro-organism can therefore be experimentally transferred from man to animals, but there is no evidence sufficient to prove that the converse can take place, for the diphtheria which affects calves and pigeons apparently is not communicable to man. Oertel, whose work marks an epoch in the diphtheria question, has objected that the experimental disease is not identical with that observed in man, but this view can hardly be sustained since, as Babes and others have shown, the histological changes in cases of spontaneous and experimental infection are identical (38). Löffler's discovery, at first received with some hostility, has been abundantly confirmed, and among the countless microbes of the mouth, nose and pharynx, some of which are pathogenic and some harmless, the Klebs-Löffler bacillus alone is capable, when present, of thriving on the mucous membrane and causing diphtheria. For other inflammations of the throat this term should be discarded, since if clinically there is a difficulty of diagnosis, a bacteriological examination may be relied upon to afford a convincing distinction between true and pseudo-diphtheria, though it may be mentioned that Bacillus diphtheriæ may exist in the mouth without giving rise to any symptoms of disease.

The morphological interest of the microbe lies in its polymorphic character which is exceedingly well marked in cultures upon eggs, and in the production of involution forms. A spore formation does not exist. The distribution of the bacillus is of considerable importance. It has been found in the secretions of the throat of children free from diphtheria as late as the twenty-fourth or thirty-first day after disappearance of the disease (9); that this was undoubtedly the specific bacillus was proved by cultivation and by inoculation experiments. Sixty-five days after all throat symptoms have vanished virulent bacilli capable of establishing diphtheria in guinea pigs have been shown to exist in the secretions of the nose (10). The demonstration of pathogenic bacteria outside the body in water, air, or upon articles of clothing, is a matter of great difficulty since form and staining behaviour are insufficient criteria, and in order to establish an absolute proof any suspected pathogenic germ must exhibit its specific action upon a susceptible organism. A proof of this nature has been given for Bacillus diphtheriæ by Park (11) and Abel (12). The former detected the microbe in the dirty linen of a patient suffering from the disease, the latter on a child's toy. Wright and Emerson (13) have also furnished absolute evidence that virulent bacilli can be recovered from the sweepings of the floor of a diphtheria ward and from the shoes of the attendants. The biological behaviour of Bacillus diphtheriæ outside the body has been exhaustively studied by Flügge (14), who has pointed out that the microbes will preserve their vitality as long as nine months. The bacilli if dried or exposed to sunlight die rapidly, and therefore currents of air cannot be a vehicle for the transmission of the disease.

The physiological behaviour of sub-cultures of the Klebs-Löffler bacillus upon agar is shown by a diminution in virulence, while an augmentation of this occurs in old bouillon cultures. Escherich (15) considers that the rapid production of acid when the bacillus is grown upon sugar bouillon tinged with litmus is evidence of virulence. When cultivated upon a medium containing peptone, Bacillus

diphtheriæ produces indol and oxidises ammonia to nitrite so that a characteristic red colour may be obtained by the addition of acid to cultures three weeks old (16). Both inside and outside the body toxins are developed, and these appear in a bacterial-free filtrate. The toxins on injection will produce diphtheria equally with the introduction of virulent bacilli, and since the inoculated micro-organisms multiply at the seat of the original lesion, and do not wander at all, or only to a slight degree with the tissues of the body (17), the bacillus belongs to that group of toxic micro-organisms which also includes the micro-organisms of tetanus and possibly of typhoid fever. From the tissues of those who have succumbed to diphtheria, as Martin (18) and others have shown, toxic substances which appear to be proteids may be recovered. The toxins of a bacterial filtrate and those separated from the dead body appear to be different in many respects. The former are considered to be ferments or enzymes, which are probably the result of the exchange of material effected by the bacillus, though according to Buchner they are disintegration products, or proteines derived from the protoplasm of the micro-organism. Notwithstanding most elaborate researches into the chemical and physical nature of the toxins or toxin of Bacillus diphtheriæ, and repeated attempts to isolate them in a state of purity, little is known beyond the specific effects which follow the injection of these substances into animals.

If it can be affirmed that a disease is caused by the invasion of specific microbes, or their products, attempts to destroy these would be a strictly scientific procedure; in other words, attempts to disinfect the living body. Quinine, salts of mercury, iodine or salicylic acid are powerful disinfectants, and also valuable drugs frequently employed in the treatment of diseases produced by the spread of bacteria in the body. In order to accomplish a disinfection of the living body numerous experiments have been made, but the results were unfavourable, until Behring and his colleagues Knorr and Boer announced that this was possible in certain diseases, such as anthrax, tetanus and diphtheria; tri-

chloride of iodine especially was found to possess a distinctly curative power. At the time this was ascertained the advocates of two rival theories as to the origin of immunity were engaged in hostile criticism. Metchnikoff, the founder of the doctrine of phagocytosis, and Behring, who held to the bactericidal properties of such fluids of the body as blood serum and lymph, were in direct scientific antagonism, which led to renewed researches into the question of immunity, and resulted in an epoch-making discovery. Behring conclusively showed that in several diseases, among which diphtheria was included, serum yielded by the blood of an animal rendered artificially immune exerted no bactericidal action upon the bacillus of the disease, but was apparently capable of destroying the toxins produced by the bacillus. Antitoxic bodies are therefore presumably present in the blood of animals which are made immune, and serum from such an animal can be both protective and curative; an already developed disease can be permanently arrested by the introduction of serum charged with antitoxins. Upon this discovery, which is undoubtedly the greatest contribution that bacteriology has at present rendered to practical medicine, rests the treatment of diphtheria by antitoxic serum. The details just briefly mentioned have been known for years, and the recent interest which has been aroused is due to the evidence adduced by Roux in favour of the value of serum as a therapeutic agent at the recent Congress of Hygiene in Buda-Pesth.

It is a purely medical question whether the mortality of the disease under treatment diminishes by antitoxic serum, but sufficient evidence has now been collected to convince the most sceptical that the subcutaneous injection of serum is a valuable therapeutic agent. The various preparations of serum obtained in this country and from abroad differ considerably in antitoxic power, and also in the dose which should be employed. A recent paper by Janowski (19) deals fully with the variations in strength of the preparations employed by Behring, Roux and Aronson. The remedy is harmless, though a transient inflammation of the skin, which may be accompanied by slight pains in the

joints, is occasionally produced. Since diphtheria is at first a purely local disease, Löffler has brought forward a method of treatment which is claimed to have had a success not inferior to that of antitoxic serum. The application of an alcoholic solution of 36 per cent. of toluol and 4 per cent. liquor ferri sesquichloratis at frequent intervals was extensively used in Greifswald during an epidemic of diphtheria in 1893-1894. Not a single patient out of seventy-one treated in this manner succumbed (20). The anti-diphtherin, proposed as a local remedy by Klebs (21), does not appear to have been followed by any results comparable to the success obtained by antitoxic serum or Löffler's fluid (22).

Behring, the real founder of serum therapeutics, has given elaborate directions for rendering animals immune. The degree to which this is possible varies in different species, but serum of great antitoxic power can only be obtained if very virulent toxins are employed. Horses, dogs, cows, goats, sheep, rabbits and guinea pigs can all reach various grades of immunity by repeated subcutaneous injections of diphtheria toxin in steadily increasing doses, a method which was devised by Ehrlich (23). Originally Behring recommended that trichloride of iodine should be mixed with the first injections, and Roux (24), who works with a toxin prepared by the growth of Bacillus diphtheriæ on a thin stratum of peptone-veal-bouillon exposed to a current of damp air, adds to the first dose one-tenth the volume of ·3 per cent. solution of iodine. The results obtained by Wernicke (25), though not of practical use, are exceedingly interesting. He has shown that dogs can reach a high degree of immunity if they are fed with the flesh of sheep dead from diphtheria, or from such as had been rendered immune. The dogs are found to yield antitoxic serum in both experiments, and this is claimed also to be efficacious in the treatment of the disease in man. A method employed by Dr. Klein is described in the March number of "SCIENCE PROGRESS" for 1895; the immunising of horses being effected by repeated injections of large doses of living virulent bacilli. Whatever method may be employed to confer immunity, a high grade is only reached after some

months, and this condition tends to disappear, but so long as immunity exists, the blood, milk and muscles of the animal yield antitoxins, which may be separated and dissolved in eight to ten times the weight of water. Beyond doubt the most valuable remedy is serum preserved in sterilised flasks. A piece of camphor should be added, and the fluid protected from light.

Human beings suffering from diphtheria may be considered to recover from the disease since the toxin of the bacillus encounters antitoxins that either pre-exist or are developed in the body as the results of the struggle of the cells of the organism against the deadly action of the diphtheria poison. Consequently, in patients who are convalescent, antitoxins should, if this view is correct, be present in the organism. In the case of typhoid fever this question has been admirably worked out by Stern (26); the serum of patients dead or convalescent from this disease possesses a destructive power upon the Bacillus typhosus and its products. The serum of persons convalescent from diphtheria is found also to be antitoxic. The experiments of Escherich and Klemensiewicz proved that such serum has a marked protective power, and more recently Rudolf Abel found five out of six convalescent patients yielded antitoxic serum (27). The efficacy of this was tested upon guinea pigs by introduction of serum subcutaneously, or into the peritoneum, and then twenty-four to forty-eight hours later a lethal dose of diphtheria toxin was administered. The antitoxic value of the serum is at a maximum about the tenth day after the membrane in the throat has disappeared. A fact, however, must be noticed which conforms with the experiments made by Stern on typhoid fever, that apparently healthy persons yield antitoxic serum, indeed five out of six who were examined. Possibly in this discovery of protective bodies in the naturally immune organism may lie a partial solution of the mystery of immunity.

The chemical and physical properties of the bodies which give to serum an antitoxic power are almost unknown. Like the toxin of the bacillus these are destroyed by heat, coagulated by alcohol, and tend to adhere to bulky

precipitates. Wassermann (28) has described an elaborate method for concentrating antitoxin from milk yielded by goats which have been rendered immune to diphtheria. The whey is separated by acidification with hydrochloric acid and rennet, then shaken with excess of chloroform and allowed to stand. By this means a clear supernatant liquid free from fat and bacteria is obtained. On treatment with 33 per cent. ammonium sulphate proteid bodies together with antitoxins are precipitated. This filtrate is collected and placed on slabs of unbaked clay in a vacuum. The excess of ammonium sulphate is pressed out of the precipitate, and this when dissolved in an amount of water equal in bulk to the original whey gives a solution ten times the original strength of the milk, so that ·9 gramme of toxin is neutralised by ·125 ccm. of the solution. Interesting as are such observations they do not essentially advance our knowledge of the antitoxin. No one has ever seen this substance, and the term itself is possibly of doubtful value.

Under Nencki's direction a renewed study of antitoxic serum has been made by Smirnow (29), who, on finding that the results obtained by the use of oxidising and reduction processes were only negative, employed a current of about 160 milliampères to electrolyse the fluid. Directly the current traverses the serum bubbles of gas develop at both the negative and positive electrode, and a turbid precipitate collects at the former. This ultimately clears up to a large extent, and an acid reaction is developed in the serum at this pole, while at the positive electrode the fluid is perfectly clear and alkaline. This observer, moreover, considers that serum-albumin in the blood is modified rather than the globulins, and after electrolysis antitoxic serum has wholly lost its power as a protective measure against diphtheria. Without throwing any doubt upon the facts which have been detailed, it is, however, most unlikely that any information as to the nature of antitoxin can be gained by such a method, for serum is a fluid of the greatest complexity, and as to the molecular structure of the proteids in that fluid absolutely nothing is known. A continuation of Smirnow's researches

is still more remarkable. Diphtheria toxin is obtained by growth of the bacillus on serum or nutrient media, in which serum-albumin or serum-globulin is the chief constituent. Toxins are produced in the first two fluids, but not in the last, since the bacillus thrives very badly on serum-globulin, and produces no toxin at all. By electrolysis of the filtrate of virulent cultures, the existing toxins disappear, and the fluid becomes powerfully antitoxic. That toxins are destroyed by a current of 500 milliampères for two hours is a fact beyond all doubt, and this destructive effect also is exhibited on enzymes, such as pepsin or trypsin (30). The introduction of this artificial antitoxic fluid is curative for rabbits which have received a lethal dose of toxin some hours previously, and this effect resembles that seen when ordinary antitoxic serum is employed. The relations which may exist between diphtheria toxin and antitoxin are supported by the evidence adduced that the more toxic the toxin, the more antitoxic the antitoxin. The latter is not destroyed by boiling, and is an effectual therapeutic remedy. These experiments have only recently been published, and they certainly do support the contention of many bacteriologists that antitoxins which do not exist in naturally immune animals such as the rat until toxins have been introduced into the body, are derived from the toxin itself (31). Moreover, the passage of a current through living cells which contain an antecedent stage of such a ferment as trypsin can effect a production of the ferment itself. Smirnow's work at any rate marks a new method of research on the nature of antitoxins, though the nature of these bodies still remains a mystery.

Researches on the toxic properties of abrin, ricin and robin made by Ehrlich proved that antitoxic bodies leave the organism in the milk. The same holds good when diphtheria toxin is used in small doses, gradually increasing in amount so as to produce a high grade of immunity in goats (32). The therapeutic value of milk is dependent upon the amount of antitoxins present, and contrasted with an equal quantity of blood the ratio is 1 : 20. Although milk

therefore has a weaker antitoxic value, the total amount of antitoxins lost in a long interval of time exceeds that yielded by blood. In a month a goat will yield 30 litres of milk, which corresponds to about $1\frac{1}{2}$ litres of blood, an amount in excess of what can be taken from the animal in the same time. The antitoxins in milk can be concentrated by Wassermann's method, and employed as a practical therapeutic agent.

The properties of the blood-serum of animals rendered artificially immune to diphtheria are not exerted upon the bacillus, but upon the toxins of this, both inside and outside the body; the effect in the organism and in a test-tube is the same. The chemistry of this reaction is not understood, but the poison is considered to be neutralised, or its action to be balanced, by bodies spoken of as antitoxins. Quantitative tests show that if a certain amount of antitoxic serum is sufficient for neutralisation *in vitro*, an amount at least five times greater is necessary when this is to counteract the same amount of toxin in the body, though it is immaterial whether the introduction of antitoxic bodies takes place at the seat of the injection of toxin or in some other part of the body. In such experiments are the bacilli or the toxins destroyed? The evidence to decide this is most conflicting. Buchner considers that the poison is not destroyed either inside or outside the body, and when protective substances appear in the blood of immune animals these bodies are themselves introduced with the toxin, or possibly are actually identical with the toxins themselves; in other words, the condition of acquired immunity is specific, and wholly different from natural resistance, a term that should be restricted to such cases as can be noticed in the rat, the blood of which animal possesses no antitoxic substances, and therefore the resistance shown to diphtheria bacilli or toxins must be fundamentally different from acquired immunity (33). That the poison is not necessarily destroyed is made clear by the following observation: Guinea pigs are treated with antitoxic serum after the introduction of a lethal dose of toxin, and these do not succumb, while the same experiment on

guinea pigs of the same weight which have undergone previous inoculations of small doses of toxin from which they have perfectly recovered causes death (34). Several deductions may be drawn from these experiments, but most probably the results are dependent upon an artificial weakening of the organism in the latter case. Upon the bacilli of diphtheria, antitoxic serum exerts no destructive power; the bacilli may even grow more vigorously upon the serum of immunised animals than upon that of normal individuals (35).

The views originally held by Behring—that "passive immunity," a term first employed by Ehrlich, which can be established by the injection of the blood-serum of an immunised animal, is a simple transport of something which has caused the immune condition—have undergone but little change since the date of his original discovery in 1890 (36). In his most recent paper (37) he maintains that specific antitoxins have only been found in the blood of immunised animals. An organism which is perfectly healthy is absolutely unaffected by injection of antitoxic serum; it is only a diphtheria-stricken organism which responds to the injection. The antitoxin of diphtheria is protective and curative only for this specific malady, and other diseases which have been treated by antitoxic serum are only benefited when the serum employed has been obtained from animals rendered artificially immune to the particular disease which it is desired to heal. The antitoxin which exists in the body arises by the action of the toxin on certain proteids of the organism. The fever and general constitutional disturbances which supervene on injection of toxin indicates that the organism attempts to actively defend itself against the entry of the poison. As the result of this antitoxins become developed, and in such an amount that not only may the toxin be rendered inert and harmless, but the excess may be utilised by transference to another animal. Curative effects can also at times be obtained by the introduction of toxins which have been weakened in virulence by chemical or physical agents, instead of antitoxic serum. This is an especially valuable treatment, not for an acute diphtheria, but for the paralytic

sequelæ of the disease, which, as is well known, do not in any way improve on giving antitoxic serum. It is impossible to doubt from this short *resumé* that Behring still holds that an essential destruction of toxin results from an accumulation of antitoxin in the body, and in the case of diphtheria the crucial experiment to decide this point is wanting, since at the present time it is impossible to separate the toxin and antitoxin which occur in one fluid. Both these bodies we recognise by their effects; by no other means can their identity be established. Allowing that they may be proteid in nature, a knowledge of them will only be possible when more extended information has been gained of the nature and constitution of proteids.

Since Behring's discovery it has been established that the serum of immunised animals is prophylactic and curative for many other diseases besides diphtheria. For many infective maladies, among which pneumonia, cholera, typhoid, hog-cholera may be mentioned, this has been abundantly proved by the researches of F. and G. Klemperer, Issaef, Pfeiffer, Sanarelli and Metchnikoff, while a recent research by Viquerat appears to show that patients suffering from acute suppuration, associated with pyogenic bacteria, may yield a serum which is curative when injected in the neighbourhood of abscesses (38). The universal application of Behring's theory of antitoxins is, however, limited, since in tetanus and diphtheria the toxins of bacilli are neutralised or destroyed, but in other diseases the serum protects not against infection with toxins, but against infection with living bacteria. In this case it is possible that the cells of the organism, even if they do not ingest and destroy the invading microbes, as Metchnikoff affirms, are roused or stimulated so as to oppose the spread of infective micro-organisms or the products of these throughout the body. In the case of protection against diphtheria the antitoxin which appears is therefore to be looked upon as the product of living cells, or as a metabolite occurring under special conditions, one of which may be the stimulation of the cell by the toxin. That antitoxins are products of living cells may possibly be inferred from the observation of F.

Klemperer, who has pointed out that immune fowls lay eggs which contain antitoxins only in the yolk, the surrounding albumin being only a cell-envelope has no antitoxic power. If the cells of the organism react, and a development of antitoxin is the expression of this, protective bodies of the same nature might conceivably arise in response to stimuli other than specific toxin. This may be a partial solution of the therapeutic effects which follow injection of antitoxic serum in cases of diphtheria. The material introduced does not act directly upon the toxin, but indirectly does so by operating as a stimulus to the cells of the organism, which are then capable of producing chemical bodies which destroy the toxin, and such substances may be antitoxic in character. This conception is largely due to Roux, and under his direction Calmette, Phisalix and Bertrand have shown that no specific action can be claimed for antitoxic serum. These observers have discovered that the serum of animals which have been rendered immune against cobra poison is antitoxic both in the body and *in vitro*. In the latter case, on warming the mixture to 70°, the antitoxin is destroyed, the toxin remaining unaltered, from which it may be concluded that the toxin remains active side by side with the antitoxin. Moreover, the serum of animals immune to rabies or tetanus is powerfully antitoxic to cobra venom. From these observations the products of cell activity which accumulate in the blood of animals immune to tetanus, diphtheria, or cobra poison, are all of an antitoxic character similar in nature, and the view that antitoxic serum is specific for a definite bacillus or its products must be modified.

The practical results of serum as a therapeutic agent in diphtheria have exceeded the most sanguine expectations. Every civilised country has already established institutes from which supplies of serum can be obtained for the treatment of this disease. Not only diphtheria, but also traumatic tetanus, which formerly was without exception fatal, has been successfully treated with antitoxic serum, and more than a hundred cases have been collected in which there is a large percentage of recovery. Enthusiasts regard

serum-therapy as the treatment of the future for infective diseases. On this point judgment must be suspended; at present it is sufficient to have established a proof that bacteriology, the youngest of the sciences which support medicine, has not only placed the etiology of many diseases upon a sound foundation, but has also contributed a marked advance in treatment.

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METHODS OF PETROGRAPHICAL RESEARCH.

IF we were required to fix an epoch from which modern Petrology might date its progress, we should perhaps with most justice select the year 1815, in which Louis Cordier produced his *Mémoire sur les substances minérales dites "en masse," qui entrent dans la composition des roches volcaniques de tous les âges.* The title itself is a landmark in the history of geology. The so-called "massive felspar" and other substances constituting the ground-mass of many lavas were, eighty years ago, generally regarded as homogeneous minerals, and the conception of "volcanic rocks of all ages" was then far from being the common-place which it is at the present day. The French geologist demonstrated conclusively that the compact ground-mass of very many porphyritic rocks is in reality only a very fine-textured aggregate of two or more minerals, and that these minerals are identical with those already familiar as porphyritic elements in the same rocks. A discovery of such moment so lucidly set forth is not easily paralleled.

Scarcely less interesting are the methods—in great measure original—by which Cordier was enabled to arrive at such results at a time long anterior to the introduction of thin slices of rocks. The microscope was for the first time systematically employed in petrological research, though only with low powers, for, working upon fragments of irregular form obtained by crushing, Cordier was compelled to sacrifice amplification to definition. The form, lustre, colour, transparency, etc., of the mineral fragments were thus studied, while other characteristics were found in the brittleness or toughness of a mineral under the pestle, the "feel" of its powder, etc. In some cases the process of "mechanical analysis" thus devised was aided by levigation in water, and by the use of a bar-magnet to separate different minerals in the pounded rock. The blow-pipe, used by De Saussure thirty years earlier, was revived and its application perfected, so as to determine with consider-

able precision the fusibility of a mineral on the Wedgewood scale; while, by a further refinement, the mutual reactions of two minerals before the blow-pipe were utilised in the identification of the minute fragments investigated.

These various methods clearly demanded considerable skill and patience, and this is doubtless one reason why the new field opened out by Cordier's memoir remained so long almost uncultivated. None the less must he be regarded as the pioneer in this line of research, and indeed some of the devices now in vogue among petrologists are no more than adaptations and improvements of those noticed above. The use of the blow-pipe in chemical and mineralogical investigations has, of course, been greatly developed, partly with the aid of special fluxes or solvents. Another kind of flame-test, closely following Cordier's lines, is the method elaborated by Szabo (1876) for discriminating the various felspars in small fragments. Here the criterion of relative fusibility is used in conjunction with Bunsen's flame-coloration tests. Szabo's method has been employed with advantage by several petrologists, and various devices have been utilised by Cole (1) and others to simplify the practice of it.

As a method of precision for identifying minerals by observation of their melting-points and their behaviour at high temperatures must be mentioned Joly's "meldometer" (2). In this the finely ground material is examined under a low power of the microscope upon a narrow platinum ribbon, which can be raised to any desired temperature by the passage of a regulated electric current. The observations may be comparative, or the actual temperature may be ascertained with considerable accuracy by means of a device for measuring the expansion of the platinum ribbon. It is evident that this instrument is capable of numerous important applications.

Coming to methods of mechanical analysis, we may note first that for Cordier's bar-magnet Fouqué (1876) and other experimenters have substituted a powerful electro-magnet, which attracts in varying degree all the iron-bearing minerals. Dölter, in particular, has shown (1882) how, by gradually increasing the strength of the current, the several

constituents of a crushed rock may be partially separated, magnetite, ilmenite, augite, hornblende, olivine, etc., being picked out successively; but this refinement does not seem to have come into general use.

Cordier's method of levigation in water is too tedious and too imperfect to be of much use in separating such minerals as felspars and pyroxenes by their not widely different specific gravities. For isolating the microscopic crystals of exceptionally dense minerals (zircon, rutile, anatase, monazite, etc.) from crushed or decomposing crystalline rocks, however, it has been used with success by some workers, *e.g.*, by Thürach, who has given an account of the process adopted by him (3). The method was originally borrowed from the miners, and Derby (4) and other workers have made use of the "batea" or washing-pan of the Brazilian diamond-seekers. In this country Dick (5) and others have used a similar device for separating the denser minerals from sands.

Notwithstanding these special applications, it is manifest that the separation of minerals by their different densities can be in general but very imperfectly effected by means of a liquid like water, much less dense than any of the minerals. To surmount this difficulty recourse has been had to special "heavy solutions," by which the majority of minerals met with can be separated hydrostatically. The two most familiar to petrologists are Thoulet's (1878), which is potassium-mercuric iodide, and Klein's (1881), cadmium boro-tungstate. Both can be prepared of specific gravities exceeding those of most rock-forming minerals, and can be diluted down as required, so that the floating mineral-grains sink successively in the order of their densities, and can be removed in turn. It is unnecessary to give in this place the methods of using these dense solutions, to describe the special apparatus for facilitating their use, or to mention other liquids which have been employed, some of superior density to the above, but with practical drawbacks. Good accounts have been given by Cohen (6) and others, and are summarised in the text-books of Rosenbusch and Zirkel.

More recently, however, Sollas (7) has devised an ingenious application of heavy liquids, which deserves to be widely known. By suitable dilution a series of Klein's solutions are prepared ranging in specific gravity, say, from 3·3 to 2·5. Equal portions of these are introduced in order, without mixing, into a vertical tube of diameter three-quarter inch or an inch. When this has stood undisturbed for perhaps twenty-four hours, it is found that diffusion has proceeded just far enough to give a column of almost uniformly graduated density from bottom to top, and so slow is the movement of the salt in solution that the "diffusion-column" so obtained can be used for several days. Into it is introduced the rock-powder, sifted, washed, and dried in the usual manner, and the constituent grains at once range themselves at various levels according to their several densities. When thus separated, they can be withdrawn by a pipette and examined. Not only is the process of isolation thus greatly simplified, but, further, the specific gravities of the several minerals are easily determined at the same time. For this purpose a series of "indicators," of suitably selected and accurately known specific gravities, are introduced into the column, where they take up their proper positions, and afford a scale of comparison. By using a graduated tube to contain the column, the specific gravity of a suspended mineral fragment can readily be interpolated between those of the two nearest indicators. These indicators may be prepared by fusing short lengths of fine platinum wire into small glass beads of various colours.

Mechanical methods of isolating the several constituents of a rock may now be considered to have reached a high degree of perfection, and indeed they have almost superseded the chemical methods, depending upon the selective action of various acids upon the different minerals, which have from time to time been practised for the same purpose. Some such chemical methods were tried and abandoned by Cordier, before he elaborated his process of "mechanical analysis," and the experience of later workers seems to show that they are not perfectly satisfactory except in some

special cases. Doubtless one reason for this is that the terms "soluble" and "insoluble," as applied to the behaviour of mineral substances with acids, are strictly of relative rather than absolute significance. One of the most successful attempts on this line was that of Fouqué (1876), who in his investigation of the Santorin lavas made use of the action of concentrated hydrofluoric acid upon the pounded rock. This readily dissolved the glassy matter and felspars, leaving the magnetite, pyroxene, and olivine almost intact. To separate the olivine from the pyroxene, he further employed weak sulphuric acid, which attacks only the former mineral. In his complete scheme of "mediate analysis" these chemical methods were supplemented by the use of the electro-magnet to separate the iron-bearing from the white constituents. Various other chemical devices have been adopted by other workers.

One main object of all methods of separation is to obtain specimens of the individual minerals pure enough for chemical analysis. The various improvements in the processes of analytical chemistry, which have given increased precision and value to results obtained in recent years, scarcely fall within our special province.

The event which has more than any other impressed a character upon modern petrographical research, and largely determined its direction during the last thirty or forty years, is, of course, the invention by Sorby (1850) of thin slices of rocks, followed by the systematic application of the polarising microscope to the study of the optical properties of rock-forming minerals. The rapid growth of interest in this branch of study and the rich harvest of results attained by its aid form an interesting chapter in the history of geology. Its progress, especially in the laboratories of the German Universities, has been sketched by Fouqué (8), Zirkel (9), Stelzner (10), Williams (11), Cohen (6), and others. In this place it will be sufficient to note a few of the more recent advances in this line of research.

Improved appliances for the preparation of thin slices of rocks need not be specially alluded to, most workers

being content to have their specimens prepared for them. There are, however, various advantages in making one's own sections, and Behrens (12) has pointed out that useful information about the constitution of a rock may be acquired during the process of polishing. Different minerals, according to their hardness and other physical properties, begin to take the polish in a definite order: spinels, zircon, tourmaline, quartz, olivine, magnetite, pyroxenes, epidote, hornblende, etc.; and some of them show at that stage characteristic appearances.

Among new instruments adapted to petrological work, Dick's new form of polarising microscope (5), (13) has so rapidly become popular that the mere mention of it will suffice. With this instrument the observer can bring into the centre of the field any small crystal in a rock-slice which he wishes to investigate, and obtain its interference-figure in convergent light without removing his eye from the ocular. There is, further, a simple device to do away with the difficulty of imperfect centring, the stage being here kept fixed, while the polariser and analyser, connected by a rack-movement, can be rotated together. Fedorow (14) has devised a somewhat elaborate instrument for the optical study of crystals, the chief feature of which is a provision for rotating the object through measured angles about three rectangular axes. The applications of this apparatus belong rather to physical optics and mineralogy, but it may also give valuable aid in the study of rock-slices. For example, in the methods of research to be noticed immediately, a crystal-section lying not far out of a particular zone which it is desired to study can be, so to speak, brought into that zone by suitable rotation.

Coming then to optical methods of procedure for the identification of minerals, we must give the first place to the discrimination of the various felspars, a problem which may be regarded as the touch-stone of all attempts of this kind. Various petrologists have made use for this purpose of the "extinction-angles" given between crossed Nicols with parallel light. In cases where crystal-grains of the felspars can be readily isolated, the well-known method of

Schuster (1880) leaves little to be desired. Cleavage-flakes parallel to the basal or to the brachypinacoidal plane are examined, and the extinction-angle determined with reference to the trace of the other cleavage. Schuster showed that the angles so obtained, with a proper convention of positive and negative directions, are perfectly characteristic of the several types of felspars. In the more general case, however, the desideratum is some means of identifying the different felspars as seen in thin slices of rocks, and often in the form of minute microlites. Fouqué and Michel Lévy attacked this problem with some success in their *Minéralogie micrographique* (1879). Their method was, in the first place, to calculate from known data, and to plot by a curve, the variation in the extinction-angle for all sections belonging to a determinate zone. For ordinary plagioclase crystals twinned on the albite law the convenient zone is that perpendicular to the brachypinacoid, and therefore to the twin-lamellæ. Sections lying in, or nearly in, this zone are easily recognised in a slice by the symmetrical extinction of the two sets of lamellæ. The extinction-angles for such selected sections may vary from zero to a definite maximum characteristic of the particular felspar examined, and measurements of three or four suitable sections will give the maximum with fair approximation. With a sufficient number of crystals cut by the slice, this test is enough to distinguish most of the plagioclase felspars; but, owing to the fact that it is usually impossible to discriminate between positive and negative extinction-angles, an ambiguity arises between the albites and certain varieties of andesine. For microlites, which are elongated parallel to the intersection of the two principal cleavages, the zone containing those cleavage-planes was investigated, but here also an ambiguity was shown to occur in the case of certain felspars. Despite these drawbacks the method can very often be applied with confidence. In 1888, and again in 1894, Michel Lévy (15), (16) rectified by the use of new data some of the maxima given in the former work. He also showed how the position of equal illumination of the twin-lamellæ affords a delicate test whether a given crystal is

cut at right angles to the lamellæ, and therefore suitable for measurement. In his latest work he goes farther, and shows that sections not lying in any determinate zone may often be utilised to give trustworthy conclusions.

To be able to determine the orientation of any random section of a crystal in a rock-slice, and to deduce the important optical constants of the mineral from it, would, of course, be of the highest importance both for the felspars and for other minerals; but this is a problem which still awaits complete solution in a practical form. Lane (17) has given formulæ which may be useful in particular cases, when the section shows the traces of known crystallographic planes (crystal-faces, cleavages, twin-planes, etc.). For instance, in a twinned augite, he measures the angles between the cleavage-traces and the twin-line, the extinction-positions of the two individuals of the twin, and their relative retardations, and (using convergent light) the direction in which the hyperbolas close into a cross; from these data can be calculated the orientation of the section, the positions of the optic axes, etc.

Recurring to the felspars, we may note another contribution of Michel Lévy (18). In 1890 he pointed out how among the random sections of felspar-crystals in a rock-slice it is often possible to verify, by tests which he notes, that some one of them is cut, with sufficiently close approximation, parallel to the brachypinacoid. If such a crystal be found, we can adapt to it the measurements of Schuster, and its extinction-angle will at once enable us to refer it to its place in the series of felspars.

In his most recent memoir, already alluded to (16), the same author has gone a long way towards solving in its entirety the problem of discriminating the various felspars in rock-slices, though it may be doubted whether some of the considerations involved are of ready enough application to come into general use. Here, for the first time, we have all the leading properties of double refraction in the felspars worked out from the most trustworthy numerical data, and graphically exhibited for seven typical varieties in as many coloured plates of stereographic projections.

These enable us, for instance, to find at once the extinction-angle and birefringence for a section of known orientation. The actual problem is, in a sense, the converse of this, and the means of solving it in numerous important cases are found to be furnished by these figures, or by the properties which they represent. Certain zones, of which that perpendicular to the brachypinacoid is the most important, are closely discussed, and it is shown that a section lying only near that zone is sufficient in general to give a result. Further, it is shown that, if a number of random sections of one kind of felspar be examined, the values obtained for their extinction-angles will tend to cluster about certain favourite numbers, which are characteristic for that particular felspar. Thus, for anorthite, the numbers most frequently found will be 32° and 41°, and the chances are three to one that any random section will give an extinction-angle over 30°; while other felspars have scarcely less characteristic properties.

In the same work Michel Lévy treats more fully of the tests by which a chance section approximately parallel to the brachypinacoid may be recognised, and the measurements by which the several felspars can be unequivocally distinguished in such a section; and he shows in addition that a slight departure from accurate orientation produces in this case very little error. He also considers sections perpendicular to each of the axes of optic elasticity and the optic axes, and shows that their extinction-angles may be utilised with advantage in distinguishing some of the felspars.

In conclusion he discusses the use of refractive indices for the discrimination of the felspars in rock-slices. A valuable paper by Becke (19) had already appeared, in which this subject is treated with much ingenuity, leading to useful practical results. Briefly his method consists in comparing the refrangibility of the felspar examined with that of quartz. It is applicable when the two minerals are in contact in the slice, along a surface which is cut nearly at right angles by the plane of section. A diaphragm being arranged to give a slightly convergent pencil of light,

the slide is thrown slightly out of focus by raising the tube, and a bright border then appears along the line of junction of the two minerals, on the side of the more refringent. Now a given section of a felspar has two refractive indices, say α' and γ', which can be separately investigated by using the polarising Nicol, and if the section has a birefringence not too low, these indices will not differ much from α and γ, the least and greatest indices of the mineral. Similarly, a section of quartz has two refractive indices, ω and ϵ', the former being constant, while by a suitable choice we can be sure that ϵ' does not differ much from ϵ. If we can find a favourable contact of felspar and quartz, which extinguish nearly in the same position between crossed Nicols, we know that either the axes of α and ω approximately coincide and those of γ and ϵ (parallel position), or α and ϵ coincide and also γ and ω (crossed position). The two cases can be distinguished by the use of a quartz-wedge or similar contrivance. In the former case we can test, by the method already indicated, whether α is greater or less than ω, and whether γ is greater or less than ϵ. In the latter case we can compare α with ϵ and γ with ω. If we can find crystals realising each of the two cases, we thus obtain four data. By reference to the known refractive indices of different varieties of felspar, Becke thus divides these minerals into six groups, which can be discriminated in this way.

It will be seen that this method is only adapted to felspars associated in the same rock with quartz (20), and that its application depends upon the occurrence of sections favourably oriented. Further, it does not distinguish between the labradorites and more basic varieties. Michel Lévy (16) has, however, extended and generalised Becke's comparison of refractive indices. His plan is, briefly, to compare the mineral to be investigated with a highly refracting liquid. To do this the cover-glass is removed from the slice, the mineral cleaned, and a drop of the liquid brought in contact with it. It can then be found which has the higher refractive index. He uses for the purpose Klein's heavy solution, diluted to have a suitable refractive

index, and for testing this he makes use of fragments of standard minerals having known refractive indices; so that in reality the liquid is used merely as a medium to institute a comparison of refractive indices between the crystal studied and known minerals.

We have hitherto said little of methods involving the use of convergent light. These have been regarded by petrographers rather as affording confirmatory tests in the identification of doubtful minerals than as being of systematic use. With Dick's polarising microscope, however, the rapid and effective application of convergent light to even minute crystals in rock-slices may often be of great service; for instance, for distinguishing quartz and felspar in the fine-grained aggregates of some crystalline schists. On the other hand, where larger crystals can be studied, the instrument advocated by Fedorow (14) has introduced a new element of precision into such measurements as those of the angles between optic axes, etc.

Several writers have pointed out how, when suitably oriented sections occur in a rock-slice, such measurements may in many cases be effected with parallel light. Lane, for example (21), calculates the optic angle of a mineral from comparison of the birefringence of sections parallel to two of the principal planes. It is evident that such methods can be of only occasional application.

There are many ways in which chemical tests may be used as an aid to the microscopical study both of rock-slices (left uncovered for the purpose) and of powdered material. Although for the isolation of minerals heavy solutions will be preferred, when practicable, to acid solvents, the latter may be profitably employed in particular cases, as, for instance, in separating augite from a basaltic rock. Again, observations of the relative rates at which different minerals are attacked by hydrochloric or hydrofluoric acid are instructive. These may be carried out by etching the surface of a rock-slice with the acid and stopping the process after a certain time; or, if the powdered rock be used, a systematic method of "fractional decomposition" may be followed, successive applications of the acid being allowed to act for

different lengths of time (12). The solutions obtained may be tested for characteristic reactions.

The results produced by etching a rock-slice can be brought out by subsequent staining with some aniline dye, which takes effect especially on the gelatinous silica liberated by the acid from some of the silicates. The presence of nepheline, for instance, can often be made evident in this way; and, by adjusting the time allowed for the etching process, other minerals may be more or less clearly brought out. Becke (22) has successfully used staining to distinguish between quartz and felspar; for instance, in the fine-textured aggregates in some crystalline schists, which are apt to present difficulties by purely optical methods. He even finds it possible to distinguish thus to some extent between the different felspars, the plagioclases taking the colour much more readily than orthoclase, while quartz remains quite colourless. Among the plagioclases, those rich in lime more readily become stained than those rich in soda, and the zonary banding so common in the crystals of many rocks can thus be rendered apparent.

When we speak of "microchemical methods," however, we refer rather to chemical reactions, carried out actually under the microscope, resulting in various recognisable crystalline precipitates. This method of examination, initiated in 1877 by Borický, has been improved by Behrens, Streng, Haushofer, Klement and Renard, McMahon, and others; and, exercised with due precautions, it is capable of giving valuable assistance to the petrologist. It can be made to yield results in some measure quantitative; to the extent, for instance, of distinguishing felspars having different relative proportions of soda and lime. A great variety of tests have been devised. In many cases it is found convenient to bring the bases sought into the form of sulphates, these being readily obtained and having often highly characteristic crystal-habits. As a rule, the form of the minute crystals is sufficient to indicate their nature, but McMahon (23) has shown that their optical properties may also be usefully employed to control the conclusions. Since the recently published translation of

Behrens' manual (12) has furnished English readers with a concise practical guide to microchemical analysis, it is to be expected that this method of investigation will find more favour among petrologists in this country than it has hitherto done.

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PROGRESS IN PHYSICAL CHEMISTRY DURING 1894.

PART I.

CONTINUITY OF GASEOUS AND LIQUID STATES.

VAN der Waals' Theory.—In connection with the theory of liquids and gases the most important communication from a physico-chemical point of view is due to Young (1), who tests the validity of van der Waals' theory of corresponding states in the case of some twenty-two well-defined and carefully purified substances. It is now beyond question that van der Waals' equation is but an approximation, and although Bakker (2) has deduced it from thermodynamical principles, Amagat's recent work (3) again shows that even in the case of compressed gases it is too simple. De Heen and Dwelshauvers-Dery (4) furnish similar evidence, as they find that, in order to make the equation satisfactorily reproduce Amagat's isothermals, different values have to be given to both constants at different temperatures. Although this is so, Young's work proves that in certain cases the theory is in surprising accord with the facts, and the results are of especial interest, as they indicate that the chemical nature of the substance must be considered in investigations of this kind.

It follows from van der Waals' reduced equation of condition that if the pressures of different substances are the same fraction of their critical pressures, then their boiling-points on the absolute scale should be the same fraction of their absolute critical temperatures, and the volumes of the saturated vapours or of the substances as liquids should be the same fraction of their critical volumes. The liquids used fall into four groups. Group I. contains benzene and its monohalogen derivatives, carbon tetrachloride, stannic chloride and ether; Group II., the three lowest fatty alcohols; Group III., acetic acid; and Group IV., the ten lowest fatty esters. The members of Groups I. and IV.

give ratios which are very nearly the same, but this is not the case for members of Groups II. and III. Now it has to be remarked that these latter liquids are all hydroxy compounds, and we can therefore conclude that if van der Waals' theory of corresponding states be tested by means of compounds other than hydroxy compounds satisfactory results are obtained.

Another deduction from theory is that if we divide the density of a substance at the critical point by the theoretical density deduced on the assumption that it behaves as a perfect gas, we ought to get a constant quantity. In the case of Group I. the value of the ratio was almost the same for each liquid, the mean being $3{\cdot}76 \pm {\cdot}04$; for Group IV. a similar result held, the mean being $3{\cdot}91 \pm {\cdot}03$. If, therefore, we confine ourselves to the same group of substances, the above deduction is very closely obeyed, although a liquid in Group IV. gives a ratio which is about 5 per cent. higher than that of a liquid in Group I. The ratios furnished by hydroxy compounds are higher still, the alcohols giving $4{\cdot}19 \pm {\cdot}19$, and acetic acid $5{\cdot}00$. The exceptional behaviour of these substances is again apparent.

Now it can readily be shown that on neglecting quantities of the second order, the value of the ratio of the critical to the theoretical density, according to van der Waals' theory, should be $2{\cdot}67$. If we take the mean of the values given by members of Groups I. and IV. we get $3{\cdot}84$. There is thus a wide discrepancy between the observed and calculated numbers. Some years ago, however, O. E. Meyer pointed out that the factor $\sqrt{2}$ ought to be used in connection with several of the quantities employed in van der Waals' theory (5), and Guye (6) was the first to show that $2{\cdot}67 \times \sqrt{2}$ or $3{\cdot}77$ is a number almost identical with the above value deduced from Young's observations on non-hydroxy compounds. The lesson which seems to flow from this work is that the agreement between theory and practice depends to a marked extent on the nature of the substances, and that the value of the generalisation of van der Waals can only be satisfactorily gauged when this influence has been more fully studied.

Critical state.--Another question having an important bearing on the theory of gases and liquids has been the subject of an animated controversy (7) during the past year. It relates to the validity of the method of determining the critical temperature and to the condition of the substance at the critical point. Batelli, Zambiasi and De Heen have asserted that the critical temperature as determined in the usual way depends on the amount of substance present in the experimental tube, although their results regarding the nature of the dependence do not agree among themselves. Galitzine found no evidence of this effect, but concluded that the meniscus disappears and reappears at different temperatures. He further makes the remarkable statement, based upon his work on ether, that at the same pressure and temperature a substance may have different densities, even if the temperature be above the critical temperature. He therefore supports the view which has been, and is still being, advocated by De Heen (8) that both liquid and gas may exist above the critical temperature. Wesendonck (9) has also described some anomalous appearances near the critical point.

In reply to statements such as these Ramsay and Young (7) recall the fact that their own work, dealing with more than twenty different liquids, gave no indication of the above anomalies. These, they point out, might easily arise if the experimental substance were not quite pure, especially if it contained air or permanent gas, or if the whole of the substance were not uniformly heated. Ramsay (10) has further described an ingenious experiment with ether near its critical point, which clearly demonstrates to what a large extent the appearances within the experimental tube are modified by slight inequalities in the temperature of the substance. Villard (11) has also shown that with specially purified carbon dioxide and nitrous oxide there are no anomalies, and there is no difficulty in determining the critical point, and Kuenen's observations (12) indicate that the presence of permanent gas is the probable source of most of the trouble to which reference has been made. It may also be noted that the critical temperature of carbon

dioxide as determined by Chappuis (13), who employs a new method based on measurements of the refractive index, by means of interference bands, is 31·4° ; Amagat found 31·35°. That two totally different methods should give practically identical values is surely strong evidence that the critical temperature is a function of the nature of the substance alone. The most weighty experimental testimony is thus in favour of the generally accepted view that at the critical point the substance is in a definite uniform condition, and that above the critical temperature one—and only one—value of the volume corresponds with a definite value of the pressure and temperature, although De Heen especially is still active in seeking evidence to the contrary (8).

LIQUIDS.

Molecular complexity.—On taking a survey of the physical chemistry of liquids for the past year, the most noticeable feature is the general application of the idea that liquids differ in respect of the complexity of their fundamental molecules. Whether liquefaction is attended by molecular aggregation has long been a puzzle to chemist and to physicist alike. To Eotvös, however, belongs the credit of first attempting to get a definite answer to the question, and it is by means of Eotvös's method that Ramsay and Shields, and Ramsay and Aston (14) have recently served to direct attention to this subject. According to the method employed it is assumed that if K, the temperature coefficient of the molecular surface energy of a liquid, be 2·121, the liquid consists of simple molecules; that if K be less, the liquid consists of molecular aggregates, and that the degree of complexity can be estimated from the value of K. In this way it is found that the great majority of liquids consist of simple molecules, but in other cases the liquid molecule is more complex than the gaseous molecule, the remarkable point being that these associated liquids, with one or two trifling exceptions, are hydroxy compounds. Here are the formulæ which are supposed to express the average molecular weight of some of the associated liquids

at ordinary temperatures — $(CH_3OH)_{2·32}$, $(C_2H_5OH)_{1·65}$, $(H_2O)_{1·64}$, $(CH_3COOH)_{2·13}$, Br_2, P_4, $(H_2SO_4)_{32}$, $(HNO_3)_2$.

Deferring for the present the discussion of the mode of estimating the degree of complexity, it may safely be said that several other physical properties give definite evidence of the presence of molecular aggregates in hydroxy liquids. From the large effect which temperature exerted on the viscosity of the acids and alcohols, and from their general behaviour as regards this property, Thorpe and Rodger (15) concluded that they consisted of molecular aggregates which decomposed as the temperature rose. Young's results have shown that hydroxy compounds do not accord with van der Waals' generalisation of corresponding states. Thorpe and Rodger (15) have also pointed out that Thorpe and Rücker's formula for calculating the critical temperature of a liquid from its thermal expansion does not apply to hydroxy compounds; this formula is based on van der Waals' theory. Guye (16) has shown that the constant in van der Waals' vapour-pressure formula has for most liquids the value 3·06, for hydroxy liquids it is larger. Now van der Waals' equation is deduced on the supposition that no molecular aggregation occurs in the liquid state, hence the large deviations of hydroxy compounds may reasonably be assigned to this cause.

Another important indication of the same thing, which, so far as I know, has not been pointed out, lies in the fact that the boiling-point of a hydroxy compound is higher than that of the corresponding sulphur compound, although the theoretical molecular weight of the sulphur compound is the greater. Alcohol, for example, has a higher boiling-point than mercaptan. On the other hand, if hydroxy compounds be excluded, the sulphur compound has the higher boiling-point; ethyl sulphide, for example, boils at a higher temperature than ethyl oxide. If we regard the boiling-point of corresponding compounds as depending mainly on the weight of the liquid molecule, the above facts indicate that, due to molecular aggregation, the molecular weight of the liquid hydroxy compound is greater than that

of the sulphur compound. Testimony of the same kind is obtained from the behaviour of solutions of hydroxy compounds in hydrocarbon solvents (*v. infra*), abnormally high molecular weights being obtained if the solutions are of medium concentration; indeed it has been proposed to utilise the properties of such solutions as a means of detecting the presence of hydroxyl in the molecule.

Guye (16) has noted other three peculiarities which, although they do not show so definitely that the disturbing factor is molecular complexity, further illustrate the exceptional behaviour of hydroxy compounds. He finds that those liquids, for which the latent heat of vaporisation reaches a maximum, are hydroxy compounds. Again, if at the same pressure we measure the densities of a substance both as liquid and as saturated vapour, for most substances the mean of the densities is a linear function of the temperature; liquids giving a curvilinear function are hydroxy compounds. As a rule vapour-pressure curves do not cut one another; the most decided exceptions are given by water, the alcohols, and acetic acid. Yet another point of the same kind is recalled by a recent investigation by Longuinine (17), who has determined the heats of vaporisation of the normal fatty alcohols at their boiling-points. According to Trouton's rule the molecular heat of vaporisation divided by the absolute boiling-point should be the same for different substances. Longuinine finds that this is true for the alcohols, the mean value of the quotient being 26·3 He concludes, however, that the value varies from series to series. A survey of the entire data, at all events, will serve to show, I think, that if hydroxy compounds be excluded, Trouton's rule appears to be very closely obeyed, considering the experimental difficulties.

Although certain properties—such as density, refractive index, and, according to Perkin (18), magnetic rotation—which are distinguished from those treated above, as they are concerned with the volume relations of atoms and molecules, give, as might be anticipated, little indication of the exceptional behaviour of hydroxy compounds, there is ample evidence of its existence, and much of this evidence

finds a plausible explanation in the supposition that these liquids contain molecular aggregates.

We now come to the question, Can the degree of complexity be estimated? and in the first place it must be stated that the method does not rest upon a firm theoretical basis. Ramsay and Shields have subjected Eotvös's theoretical views to adverse criticism, and although this is affected by a misconception (19) due to the fact that Eotvös does not use the term "corresponding temperature" in the sense employed by van der Waals, it must be admitted that Eotvös's proof is not rigorous. Ramsay and Shields do not attempt to give a proof, but strive to show that the mode of estimating the molecular weight of a liquid from the rate of change of its surface energy is strictly analogous to the mode of estimating the molecular weight of a gas from the rate of change of its volume energy. Now the latter method presupposes that we can calculate volumes of different gases, the volume of energy of which is due in each case to the same number of molecules, and if in a similar way we could ascertain for different liquids areas of liquid surface, the surface energy of which is due in each case to the same number of molecules, then the analogy might be valid. In the present state of the theory of liquids, however, it seems to me that we do not know how to estimate areas of different liquid surfaces satisfying the above condition. The area which has been used is the molecular area, or an area upon which there lies on the average *in the interior of the liquid* the same number of molecules. But although this is so, it does not follow that the surface energy possessed by the molecular area, in the case of different liquids, is due to the agency of the same number of molecules. For, in the first place, it is certain that the distribution of molecules on the surface will not be quite the same as on a plane in the interior of the liquid, and in the second place, how can we tell, speaking roughly, that in the case of one liquid one layer of molecules, while for another two layers, etc., are not operative in producing the surface energy? The number of molecules participating in the surface energy depends not only on the area of the liquid surface, but also on the sphere of action of

the molecule, which in turn depends on the distance at which it can attract its neighbours.

Inasmuch as Ramsay and Shields' analogy cannot be justified until these points have been disposed of, it seems to me that, even on neglecting other reasons, such as discrepancies between the testimony of viscosity and surface energy, no stress should be put upon the actual values of liquid molecular weights as deduced by the method at present employed.

Vapour-pressure and boiling-point. — The vapour-pressures of the fatty acids have been determined by Kahlbaum (20), who finds that the statical and dynamical methods give the same results. Landolt's statical observations, which have long been quoted as supporting the opposite conclusion, are shown to be erroneous, probably because his liquids were neither quite dry nor air-free.

Batelli's statement that at constant temperature the observed value of the vapour-pressure depends on the relative volumes of liquid and vapour present in the experimental tube has been tested by Young (21) in the case of iso-pentane. Over wide variations in the ratio of the volumes there was no indication whatever of this effect.

Wirkner (22) has measured the vapour-pressures of a number of aromatic compounds. In several cases the curves cut one another, and he finds that none of the usual vapour-pressure formulæ satisfactorily represents the facts. A new and complex formula, involving the heat of vaporisation and the specific heats of the vapour, has been devised by Krævitch (23), but it is little suited for general use.

A matter of practical importance, which is also treated theoretically, has been taken up by Barell, Young, and Thomas (24), who deal with the separation of three liquids by fractional distillation. Applying F. D. Brown's views to the case of three liquids, after making assumptions regarding the constants in the formulæ, they find that if a mixture of three liquids, A, B, C, having increasing boiling-points, be fractionated, the lower fractions soon consist of A and B, and the higher of B and C. These may be fractionated in the usual way. This result is verified in the case of a mixture of methyl, ethyl, and propyl acetates.

A lengthy discussion on the law of corresponding boiling-points has been initiated by Duhring (25), who maintains that his law has been ascribed to Colot by Young. The only point of importance which has arisen is due to Kahlbaum and Wirkner, who show, as Duhring himself has admitted, that the specific factor in his formula is not independent of the temperature.

A new formula, connecting the boiling-points of homologues, has been put forward by Walker (26). It is based on the view (due to Burton) that the percentage difference in the boiling-point of two members of a series is proportional to the percentage difference in their molecular weights. It is of the shape $T = a\ M^b$, where T is the absolute boiling-point, M the molecular weight, and a and b are constants varying with the series. The formula applies to a large number of series, but not to the alcohols, and the alkyl bromides and iodides. Without exception, the initial members of series do not agree with the formula. That the boiling-points of initial members is anomalous has long been known, and many other physical properties give evidence of the same kind of irregularity, particularly magnetic rotation, viscosity, and melting-point. It is even noticeable, according to Eykman's recent work (27), in the case of refraction and dispersion.

Cohn (28) has attempted to trace stoichiometric relationships in the case of certain boiling-points. He finds that corresponding normal propyl and allyl compounds have the same boiling-point, and that if two acids form a ketone, containing normal alkyl radicles, CO_2 being eliminated, the boiling-point of the ketone is 178° lower than the sum of the boiling-points of the acids. Of the other relations he obtains the most noteworthy are, that an aldehyde boils at the same temperature as the amine with the same number of carbon atoms in the molecule, and that the displacement of phenyl by carboxyl does not alter the boiling-point.

Viscosity.—For the past four years Thorpe and Rodger (15) have been engaged on the study of the viscosity of liquids, and an account of their work was the subject of the Bakerian lecture for 1894. Observations were made on over seventy liquids at temperatures between 0° and the

boiling-point. As regards the effect of temperature on viscosity, it varies to a remarkable extent with the nature of the liquid, and is most marked in the case of hydroxy compounds, particularly the alcohols; indeed, both as regards their large viscosities at low temperatures, and their large temperature coefficients, the higher fatty alcohols foreshadow the well-known behaviour of the glycols, glycerin, and other polyhydric alcohols. The most generally useful formula for connecting viscosity and temperature is that of Slotte, $\eta = c(1 + bt)^n$, where η is the viscosity coefficient and c, b, and n are constants varying with the liquid.

In attempting to correlate viscosity and chemical nature the authors determine, at different series of comparable temperatures, values of the molecular viscosity, and molecular viscosity-work. The former is the product of the viscosity coefficient and the molecular area, and is the viscosity referred to a surface upon which there lies in the case of different liquids the same number of molecules. The latter is the product of the viscosity coefficient and the molecular volume. The comparable temperatures used are the boiling-point, the corresponding temperature of van der Waals, and the temperature of equal slope. The last is the temperature, varying with the liquid, at which temperature is in each case exerting the same effect upon the viscosity. The most definite stoichiometric relationships are obtained at this new system of comparable temperatures. By giving definite values to the different atoms and modes of atom-linkage, such as iso-linkage, double-linkage, and the ring-grouping of atoms, it is possible to calculate values of the molecular viscosity and molecular viscosity-work, which closely agree with those actually observed. Chemical constitution has a marked effect; for example, on keeping the values of carbon and hydrogen the same, widely different values have to be ascribed to carbonyl-, ether-, and hydroxyl-oxygen. The values for hydroxy compounds differ greatly from those of other oxy-compounds, and together with irregularities which they exhibit amongst themselves, give evidence of molecular complexity. One important point is that the relationships obtained between the viscosity con-

stants at any one value of the slope are the same as at any other. Results of such a general character have not yet been obtained by the use of other comparable temperatures, and suggest the use of temperatures of equal slope in the case of other properties, especially if these, like viscosity, are largely affected by temperature.

De Haas (29) has measured the viscosity coefficient of methyl chloride between its boiling-point and critical temperature, and Kamerlingh Onnes (30) has used the values obtained together with those of Warburg and Babo on carbon dioxide to test his theory that corresponding states are to be considered as mechanically similar forms of motion. According to this theory, at corresponding temperatures, for two liquids A and B

$$\eta_A : \eta_B = (\sqrt{M}/\sqrt[6]{\theta/\pi^4})_A : (\sqrt{M}/\sqrt[6]{\theta/\pi^4})_B$$

where M, θ, and π are respectively the molecular weight, critical temperature, and critical pressure. Near the critical temperature the theory is justified. The theory also indicates that if ϕ be the critical molecular volume, $\eta\sqrt[3]{\phi^2} / \sqrt{M\theta}$ and $\eta\sqrt[6]{\pi^4} / M^3\theta$ should be constants at corresponding temperatures. Using the values for η given by Pribram and Handl and earlier observers, this is found to be approximately true for some forty liquids at the temperature of ·58. The acids and the alcohols especially give large deviations.

Völlmer (31) has tested the rule that at the boiling-point the product of the heat of vaporisation and the molecular volume is proportional to the square root of the viscosity coefficient. For water, methyl and ethyl alcohols, this seems to be the case, but ether and benzene give large deviations of opposite signs.

The viscosity of fused sulphur has been studied by Brunhes and Dussy (32). It diminishes up to a temperature between 156° and 157°, then increases, and at 162° is so large that the substance could not be made to flow through the capillary tube employed.

Refraction and dispersion.—In connection with refraction and dispersion the most extensive research is that of Bruhl

(33) on tautomerism. The aim of the work was to ascertain the constitution of substances which might either contain the group :CH·CO· or :C:C(OH)·, and also to find whether a substance might not exist partly in the one form and partly in the other, the relative amounts varying with the temperature. It was found that ordinary fatty and aromatic ketones, diacetyl, dipropionyl, and acetonylacetone, the alkyl derivatives of the acetoacetic esters, acetylformic and acetylacetic acids are true keto-compounds. The observations extended also to derivatives of camphocarboxyllic, malonic, and ethyl-malonic acids, etc.

In general, where the comparison is possible, the results obtained for the constitution of the substances at ordinary temperatures agree with those deduced by Perkin (34) from his work on magnetic rotation. This is, however, not in general the case as regards the effect of temperature. Perkin found that all diketonic compounds of the fatty series exist, partly at least, in the hydroxylic condition, and that as the temperature rises gradual change into the ketonic modification takes place. In the case of acetylacetone and ethyl acetone oxalate, for example, Bruhl concludes on the other hand that the constitution is independent of the temperature. The methods which have up till now been used in estimating this alteration consists in finding whether the molecular refraction, dispersion, or magnetic rotation varies with the temperature; because these constants are greater for unsaturated than for saturated compounds. But even in the case of stable substances the molecular refraction and magnetic rotation vary to some extent with the temperature, hence their indications of tautomeric change are always more or less uncertain. In his paper Bruhl relies on the indications of dispersion alone, as it is highly influenced by constitution, and for a stable substance is little altered by the temperature. It is to be hoped that a more minute study of the effect of temperature on the optical constants of stable substances will serve to explain the above discrepancy, and put upon a firm basis what promises to be one of the most beautiful applications of physical methods to chemical problems.

Laar put forward the view that the structure of a tautomeric compound is not definite, but is continually oscillating from that of the one to that of the other tautomeric form. Bruhl concludes that this view cannot hold for fatty compounds, although it may be true for aromatic compounds.

In another lengthy communication (35) Bruhl discusses the constitution of benzene in the light of physical evidence. He compares the densities at 20°, the molecular volumes, and molecular refractions, of benzene and its di-, tetra-, and hexahydrides, and of hexane, hexylene, diallyl, and dipropargyl. The constants of the fatty compounds always differ from those of their aromatic isomers, and the alteration in the constants produced on passing from benzene to its hexahydride is best explained by assuming that each addition of H_2 corresponds with the loss of a double-linkage, and that on passing from benzene hexahydride to hexane, the large alteration in the physical constants is due to the breaking up of the ring and the formation of a straight chain. It is therefore concluded that Kekule's oscillation formula best expresses the constitution of benzene, and it is shown that thermal data may be interpreted as pointing to the same conclusion. Bruhl considers that the structure of benzene is best represented by Sachse's model. This is a regular octahedron with two parallel faces removed, six regular tetrahedra having been placed on the six remaining faces. The carbon atoms are supposed to be at the centres of the tetrahedra, and the hydrogen atoms at the six apices of the model. Kekule's formula is the best plane representation of this configuration.

It is well to bear in mind, as Ostwald points out (36), that the above treatment of the subject is in reality based on analogy; although it must be admitted that if the attempt be made to apply the conceptions of double and single bonds, Bruhl's conclusion is the most satisfactory.

Mond and Nasini attributed the high molecular refraction of nickel carbonyl to the metal. Gladstone, however, considers that the cause is to be found in the peculiar arrangement of the carbonyl groups, and Armstrong has suggested that when several of these are present in the molecule they exert

a co-operative effect in increasing the refraction. Nasini and Alderlini (37) have measured the refraction constants of non-metallic substances containing several groups, but find the values are normal. It is thus indicated that the high values of metallic carbonyl compounds are due to the metal.

Nasini and Carrara (38) consider that furfuran and pyrazole, etc., have a centric structure. Refraction constants have also been determined for furfurylic alcohol, pyromucic acids and its salts (39), and for some organic phosphorus compounds (40), but have led to no general results.

Rotation of the plane of polarisation.—Most of the work on optical activity may be grouped around Guye's theory. Miss I. Welt (41) has measured the rotatory powers of hydrocarbons containing the active amyl radicle. Ethyl-propyl and isobutyl-amyl have almost the same rotatory powers, the values being about half that of diamyl. The facts accord with the views of Guye and Gauthier. The rotatory power slightly diminishes as the temperature rises. In the case of the ethereal glycerates and diacetyl glycerates, on the other hand, as in the case of the tartrates, Frankland and McGregor (42) find that the rotatory power increases with the temperature. In general their results do not accord with Guye's theory. They find that in the series of diacetyl glycerates the homologue with the maximum rotatory power is lower in the series than the salt with the heptylic radicle; according to theory the salt with the C_{13} radicle should have the maximum value. Since methyl and ethyl diacetyl glycerates contain groups of equal mass attached to the asymmetric carbon atom, they ought to be inactive; both are, however, powerfully active. Again, the alteration in the rotatory power produced by substituting acetyl, propionyl, and benzoyl, for the hydroxylic hydrogen of methyl glycerate, is not in accord with theory. Walden (43), who has dealt with twenty-six derivatives of active amyl alcohol, and Piutti (44), who has worked with derivatives of asparagine, come to the same conclusion as Frankland and McGregor, namely, that the nature as well as the mass of the radicles attached to the asymmetric carbon atom profoundly influences the rotatory power.

It is noteworthy that more attention is being paid to the influence of temperature. This effect is most remarkable, as in some cases the rotatory power rapidly increases as the temperature rises. Colson (45) has made experiments to show that this may be due to decomposition of the substances. Le Bel (46) finds, however, that in the case of methyl and ethyl tartrates the change is not due to the presence of acid or alcohol, nor, according to Ramsay's measurements, can it be ascribed to alteration in the molecular complexity of the liquid, at any rate above 70°.

Several observers are now using in place of the old measure of the molecular rotation, the molecular deviation proposed by Guye, which is the product of the angle of rotation for unit length and the cube root of the molecular volume. It is questionable how far this is an advantage. For although the old measure is not all that could be desired, on theoretical grounds the molecular deviation can hardly be held to be an improvement. As I have pointed out (47), it would only give the effect produced by the same number of molecules of different liquids, if the region within which the ray could be influenced by a molecule were proportional to the molecular volume, and for this there is no support in fact. Of course in the present state of the question the agreement with observation is the best test of the worth of either formula. Since there is little to choose between them on this score it is to be hoped that observers will not disregard the old measure until more light has been thrown upon the question.

On account of the increased rotation, measurements of optical activity would be much enhanced in accuracy if light of shorter wave-length than D-light could conveniently be obtained. Landolt (48) has recently described a series of absorption cells which on passing white light through them give beams of different colours. The light thus obtained is not strictly monochromatic, but appears to give the same rotation as light of a definite wave-length.

Another important practical point is the modification of Lippich's polarising prism (49). Instead of using one auxiliary Nicol he now uses two, the field of view being

divided into three parts, the intensity of the outer portions being the same in all positions of the analyser, and of course equal to that of the middle portion at the zero position. Greater accuracy is obtained with this arrangement than when the field is only divided into two parts.

Dielectric constant.—An investigation of a property little studied from a physico-chemical point of view, namely, the dielectric constant or specific inductive capacity, has been carried out by Thwing (50). He uses a method, suggested by Hertz, based upon the resonance of electrical oscillations. Most of the observations were made at 15°, but in the case of water they extend from 0° to 90°, and exhibit a well-marked maximum at 4°. If K, M, and D be respectively the dielectric constant, the molecular weight, and the density, the results show that MK/D may be calculated from definite partial values corresponding with the atoms and groups of atoms composing the molecule; the agreement between observed and calculated values being, in general, satisfactory.

A remarkable relationship, which held for more than twenty hydrocarbons and solid substances, is that K is 2·6 times the density. It is somewhat surprising that more definite relationships appear to be obtained by the use of MK/D than have hitherto been obtained by the expression $M(K-1)/(K+2)D$ (51).

The above remarkable results will probably serve to direct attention to this property, several points in connection with which require reinvestigation. According to Maxwell's theory, $\sqrt{K}$ should be equal to the refractive index for rays of infinite wave-length. Using for the refractive index the first term in Cauchy's dispersion formula, Jahn and Möller (52) have shown that for several substances this is not the case. Again, according to the Lorentz and Lorenz formula $(K-1)/(K+2)$ for a given substance should be proportional to the density. Rontgen (53) finds however that K for water or alcohol is practically unaltered even at pressures of 300-500 atmospheres. There are now several methods of measuring K, and a new one has just been described by Nernst (54). There is, therefore, every opportunity for attacking these questions afresh.

SOLIDS.

As illustrating the relations between solids and liquids, the observations of Dewar and of Spring are especially interesting. Dewar (55) finds that under a pressure of sixty tons per square inch many solids flow through a narrow tube, and behave as highly viscous liquids, while other solids show no signs of flowing. The tube used was half an inch long and one-sixteenth of an inch in diameter. Organic and inorganic substances were employed, but no relation between the chemical nature of the substances and this property of flowing could be traced. For example, although potassium chloride and caustic soda flow and form a wire, this is not so in the case of sodium chloride and caustic potash.

Spring's experiments (56) consisted in clamping two cylinders of metal end to end and heating to 200° or 400°. In from four to eight hours he found the cylinders became continuous, and if they were originally of different metals, an alloy was formed, it might be for 18mm. in the region of the junction. He concludes from these experiments that even below the melting-point there are indications of the liquid state; the velocity of certain of the molecules is as high as the mean velocity of those of the liquid substance.

Periodic law.—Three inquiries may be noted in connection with the periodic law. Töpler (57) finds that the volume-change observed when a metal melts is a periodic function of the atomic weight. Bailey (58) points out that in an "even" series of elements the temperature of decomposition of an oxide is higher the higher the atomic weight, in "odd" series the reverse rule holds. According to Deeley (59) if the density of an oxide be divided by the atomic weight of the contained metal the quotient is a periodic function of the atomic weight.

Melting-point.—Cohn (28) finds that the melting-point of a ketone, when an even number of carbon atoms is present in the molecule, is 8° lower than that of the corresponding acid, and that if an odd number of carbon atoms be present the melting-point is 14°-15° lower. He also investigates the melting-points of several "odd" and "even" series of substances; for the substituted malonic acids the

ordinary rule is not obeyed. Béhal and Choay have determined the melting-points and boiling-points of a number of phenols and their derivatives (60).

As regards methods, V. Meyer, Riddle, and Lamb (61) have improved the method of Meyer and Freyer for determining the melting-points of salts. This method involves the use of a platinum air-thermometer. The platinum resistance-thermometer of Callender and Griffiths has also been used by Heycock and Neville (62) to determine high-temperature melting-points, particularly those of metals. So far as the results go these two methods give fairly concordant values. The latter method especially promises to be of considerable value in this field. For rough work over the temperature range from 200° to 600° or so, the thermometer described by Baly and Corley (63) containing sodium-potassium alloy in place of mercury may also be found of service, although as the alloy attacks the glass the readings in time become troublesome to make.

Heat of fusion.—The heats of fusion of a number of organic compounds have been measured by Bruner (64). The value for a brom-derivative is greater than that of a chlor-derivative. As a general rule his numbers agree with those deduced from observations on the freezing-point of solutions by van't Hoff's formula, unless in the case of palmitic acid (found 39·2, calc. 49·5) and α-naphthylamine (found 22·3, calc. 26·3).

Vapour-pressure of salts.—According to Bailey (65), even at temperatures below the boiling-point a dissolved salt has an appreciable vapour-pressure, and consequently if a saline solution be evaporated, there is a small loss due to volatilisation of the salt. Special pains were taken to prevent the possibility of the salt being mechanically carried over. The salts examined were chlorides of the alkalies, and the loss was found to be greater the greater the molecular weight and the stronger the solution. On evaporating a litre of a solution containing 286 gr. of cæsium chloride, 18·86 mg. of salt were lost.

Stoichiometry of glass and crystals.—Winkelmann and Schott (66) find that the physical properties of glass are functions of its chemical composition, indeed their experiments

make it possible to calculate the elastic properties of glass to within 8 per cent. from a knowledge of its composition.

Valuable information regarding the stoichiometry of crystalline substances has been obtained by Tutton (67). He has studied the isomorphous series consisting of potassium rubidium and cæsium sulphates. Both as regards the angular measurements of the crystals, and the development of the faces, and also as regards their optical behaviour, molecular volume, etc., the properties of the rubidium salt stand between those of the potassium and cæsium salts, and approximate more nearly to those of the potassium salt.

That simplicity in the chemical structure of a substance is correlated with its crystalline form, according to van't Hoff (68) was pointed out by Buys-Ballot in 1846. Retgers (69) has summarised the nature of the evidence, and finds that 85 per cent. of the elements, 88 of the diatomic compounds, and 53 of the triatomic crystallise in the regular and hexagonal systems; whereas the majority of complex organic and inorganic compounds crystallise in the rhombic and monoclinic systems.

Surawicz (70) states that the hydration of a substance is usually attended by a fall in the symmetry of its crystalline form; its specific gravity and hardness diminish at the same time.

Phosphorescence.—The phosphorescence of solids at low temperatures has been studied by Pictet and Altschul and by Dewar. The former (71) find that in the case of sulphides of the alkaline earths phosphorescence ceases at 67°. Dewar (72) finds that, in general, substances which feebly phosphoresce at ordinary temperatures become more active at low temperatures. The substances were cooled by immersion in boiling liquid air, all organic substances being solid under these conditions. They were then exposed for a short time to the light of the electric arc, and viewed in a darkened room. At low temperatures the substances seem capable of absorbing in an increased degree light energy which is emitted as phosphorescent light as the temperature rises. Amongst inorganic substances the platino-cyanides, and amongst organic substances ketonic compounds, exhibit the most marked phosphorescence.

J. W. RODGER.

NOTES ON THE REPRODUCTIVE ORGANS OF OLIVE-BROWN SEAWEEDS.

THERE has been a good deal of speculation in recent phycological literature on the subject of the conceptacles and the cryptostomata (Fasergrübchen), or sterile or neutral conceptacles, as they are variously called, which occur in certain orders of olive-brown seaweeds. In the discussion of this subject, and the search for explanations of the puzzles it freely offers, there has been shown a disposition to restrict the evidence and the argument to the comparison of development of these bodies in the different orders in which they occur. It would be out of place and mischievous to disparage this method and to seek to detract in the least from its value, but the exclusive employment of it reminds one of the attitude of the observer who sought to explain the movements of a semaphore by assigning them to the caprice of the signalman without reference to any trains that might happen to be running. The things themselves have been exhaustively described and compared, and the questions have been asked: (1) Are the cryptostomata abortive conceptacles? (2) are they the older of the two, and have they come in time to bear reproductive organs? Authors have been found to answer both these questions with yes or no, while a third takes the view that they are "of equal antiquity, and that neither is the outcome of the other". Where these answers are not mere guesses, they are founded on a cursory glance at the neighbouring forms, or on speculations as to possibilities in the ancestors of the *Fucaceæ* and *Laminariaceæ*. Since none of these ancestors are known to us, and do not appear to be likely to meet the delighted eye of the botanist, at all events in a condition fit for the microtome, it is probably more likely to be fruitful if we extend the area of our inquiry among the living forms more or less related to those discussed. To vex ourselves about ancestral forms in this case is very much like crying for the moon.

The constants of the case are these. The *Fucaceæ* have their reproductive organs buried in more or less round, flask-shaped pits beneath the surface called conceptacles, where they occur among hairs—paraphyses. Often on the same species there occur pits of precisely the same mode of development which contain the hairs, but no reproductive organs. These barren pits are what have been termed the sterile or neutral conceptacles, Fasergrübchen, cryptostomata, etc. The development of these conceptacles was first accurately investigated by Professor Bower (1). His observations were greatly extended by Oltmanns (2), who described their occurrence in many other genera of *Fucaceæ*. Miss Barton (3) added to this, and discussed the subject further (4) in its later developments. In their investigation of the remarkable type *Splachnidium*, for which they founded a new natural order, Miss Mitchell and Miss Whitting (5) discovered a new kind of conceptacular body, developing after a fashion of its own, and containing not oogonia and antheridia like those of *Fucaceæ*, but sporangia like those of *Laminariaceæ*. It is a different kind of conceptacle, but yet clearly comparable with that of *Fucaceæ*. The present writer (7) next investigated the barren cryptostomata of three Laminarian genera, and found them different from but comparable with those of *Splachnidiaceæ*. The interesting point now comes in, though of course it has been known for a long time, that the Laminarian cryptostomata are always barren, and that the ordinary occurrence of sporangia in this order is in patches or sori where they are mixed with paraphyses, quite apart ordinarily from any cryptostomata. In one of the genera, however (*Adenocystis*), these pits occur right in the middle of the sori, but are themselves barren. About the same time and working in the same laboratory Miss Mitchell (6) found a simple form of pit or cryptostoma in another order (*Encœliaceæ*) in the genus *Hydroclathrus*, also in the middle of sori this time of plurilocular sporangia. Miss Barton has noted the occurrence of other pits of the kind on the barren thallus of *Chnoospora* (*Sporochnaceæ ?*) and they have been long known as very shallow pits on

such forms as *Punctaria*. There is here a great range of different kinds of pit or cryptostoma developing in different ways, and it may be objected that I am casting my net too widely, and bringing together things that do not sufficiently resemble each other. That will be justified or not by further considerations; in fact this diversity itself will help us, I venture to think, to a better understanding of the difficulties. It is characteristic of a large number of the olive-brown seaweeds to have hairs associated with their sporangia or other reproductive bodies; in fact the sporangia are themselves morphologically hairs or branches of hairs. The hairs that are sterile or vegetative, fulfil among other functions that of furnishing protection or shelter to the sporangia—protection it may well be against assaults of minute animals and the like, or against the force of currents that might prematurely detach the sporangia, or even against excess of light. In the most simple filamentous forms the hair-like branches themselves act in this way, while the genera with stouter shoots have their sporangia either immersed in the substance of the thallus, or associated with dense tufts of hairs, or sunk in pits (conceptacles). In short, they exhibit after one fashion or another a tendency to conceal the developing reproductive bodies. This tendency finds its highest expression in the development of conceptacles, and we accordingly find in the most highly differentiated order of the group, *viz.*, the *Fucaceæ*, the most perfect example of conceptacle.

If we may look for an illustration elsewhere of the view I wish to state, it has been well said of the Ascomycetes, among the fungi, that the flasked-shaped perithecium is the same thing as the basin-, or flat disc-shaped apothecium with the edges curled up. If we regard the sori of olive-brown algæ in the same way, the conceptacle of *Splachnidium* is much the same thing as a Laminarian sorus with its edges curled up. I was so much impressed with this simple view of the matter some years ago that it has led me, with the help of fellow-workers, to make as minute a study as material has permitted of the Laminarian sori and cryptostomata, and of these bodies in other orders.

The discovery of cryptostomata in the sori of *Adenocystis* and *Hydroclathrus* seemed to point to rudimentary conceptacles, or, if it be preferred, ancestral ones. This evidence might be made to fit without violence into the general scheme of seeking shelter of the kind for reproductive bodies. We have, however, to reckon with the fact that in other forms the cryptostomata occur apart from the sori, and it is precisely this kind of obstinate fact that shows us the futility in the present state of evidence of guessing at the relative antiquity of conceptacles and cryptostomata. If anything it favours Miss Barton's view that they are "of equal antiquity, and that neither is an outcome of the other".

The search, however, among the Laminarian sori for evidence of curling up, of seeking the shelter so provided, has been rewarded in the cases described by Miss A. L. Smith and Miss Frances Whitting (8). The sporophyllous leaves of *Postelsia* and the gigantic *Macrocystis* are furrowed longitudinally with parallel trenches, and it is within the shelter of these trenches that the sori of sporangia are placed. So perfect is this adaptation that a transverse section of the leaf (see plate xx., figs. 2 and 5 of their memoir) would appear to show the effect of a series of conceptacles like those of *Splachnidium*. Of course this appearance is shown only in transverse section, and proves nothing more than that it is an adaptation to the same end as a conceptacle, of a less perfect kind probably, at all events of a simpler kind.

I have cited these instances and considerations with no pretence of offering an adequate explanation of the puzzles to be found in this subject, but rather with the hope of showing that the conceptacles and cryptostomata of the *Fucaceæ* are not isolated phenomena, but part merely of a series showing the same character and tendency, and called forth to meet like requirements.

Recent attempts to classify the orders of olive-brown algæ have been characterised for the most part by too much being made of the differences between them. This is a very natural thing under the circumstances, but it is occasionally well for us to dwell rather on the resemblances,

and to ascertain whether, after all, the gulfs that have been fixed between certain orders are so wide as we are prone to believe. But for the absence of conceptacles, to which perhaps less weight may be attached from considerations I have submitted, the male and female sori of *Cutleriaceæ* have a strong resemblance to those of *Fucaceæ*. There is the further deeply interesting fact of the occurrence of non-sexual sporangia in this order, a mode of reproduction absent from the *Fucaceæ*. The unfertilised oosphere is ciliated unlike that of the *Fucaceæ*, but it is not impregnated until it has come to rest, and it is considerably larger than the antherozoids. It is customary to mark off these groups (and sometimes the *Tilopteridaceæ* with them) from the *Phæosporeæ, i.e.*, the remainder of the olive-brown sea-weeds (except *Dictyotaceæ*), and for purposes of classification this is of course necessary, but among the *Phæosporeæ* interesting types emerge which suggest at least continuity. The genus *Myriotrichia* (9), for which it is difficult to find a proper home, has unilocular sporangia of the ordinary kind, but its plurilocular sporangia, which give rise to the conjugating gametes, are exceptional. There are differences of size among them, and this difference is but the outward expression of the nature of their contents. As a rule the small sporangia (or gametangia) give rise to four large gametes, and the others to eight, but the number varies from six to twelve. The interesting point is that conjugation takes place only between a large gamete and a small one, and apparently either while motile or at the moment of coming to rest. The large one appears to absorb the small one, and soon nothing but the two pigment spots remain to mark their former separate existence. We have here a preservation of the difference of size. Looked at simply from the point of view of conjugation *Cutleria* is a link between the types of *Fucus* and of *Myriotrichia*. The better-known case of *Ectocarpus siliculosus* offers another exception to the rule of equal conjugation of gametes. Here the female gamete first comes to rest, and is then surrounded by numerous male gametes, one of which succeeds in conjugating with the female

gamete. That it should first come to rest recalls *Cutleria* again, and in part *Myriotrichia* also.

The *Ectocarpaceæ* supply us in fact with quite a crop of aberrant forms, puzzling to the systematist, but of the highest interest from our point of view. In *Ectocarpus secundus* and *E. Lebelii*, recently investigated afresh by M. Bornet (10), there occur bodies to which we cannot hesitate to apply the term antheridia. Considering other resemblances between *Tilopteridaceæ* and *Ectocarpaceæ* this matter has a particular interest. The antherozoids completely resemble those of *Fucus*, *Cutleria* and *Tilopteris*, and we must inevitably regard them as possessing the same potentiality. The absence of a chromatophore and of reserve-material in their protoplasmic contents points to an incapacity for further development. The so-called zoospores of these species are almost as much greater than these in size, as the ciliated oosphere of *Cutleria* is greater than its antherozoids.

Another species of *Ectocarpus*, *viz.*, *E. pusillus* Griff. (not *E. pusillus* Kütz, in which Goebel has observed conjugation—the latter is properly called *E. globifer*, as Bornet has shown), starts another train of reflections. The spores (at least those of the plurilocular sporangia) have no cilia, and are immobile. This latter character does not necessarily point to the *Tilopteridaceæ*, as has been held, since the unilocular sporangia of *E. pusillus* contain a number of spores, and the unilocular bodies of *Tilopteridaceæ* have but one spore (or oosphere, as the case may be). The loss of active mobility, however, recalls the cases of the oospheres of the *Fucaceæ*, as well as the presumptive ones of *Tilopteridaceæ*, and of all three kinds (male, female and non-sexual) in the *Dictyotaceæ*. In *Tilopteris* and *Haplospora* the so-called oosphere is clothed with a membrane before it is set free, but in *Scaphospora* the membrane is not secreted until after it is set free. If we regard these bodies as oospheres, the objection arises that they are set free, in two of the genera, enveloped in a membrane, but it should be remembered that the oogonia of *Pelvetia* (*Fucaceæ*) have a persistent inner gelatinous membrane which does not prevent fertilisation.

The absence of active mobility, however, is most interesting when we come to consider the case of *Dictyotaceæ*. Some authors have sought in them a link with the *Florideæ*, and most now go so far as to assign them a place apart pointing towards *Florideæ*. This view is based on the unciliated character of all the reproductive bodies, the resemblance of the motionless antherozoids to the spermatia or pollinoids of *Florideæ*, and the division into four of the spores constituting a likeness to the tetraspores of the same group. The contention really rests on no more than this slender support, and the absence of any observation of fertilisation leaves the field open for speculation. We have seen in *Ectocarpus pusillus* a lack of mobility in the contents of the plurilocular sporangia which is a fair parallel to the motionless antherozoids, if I may so term them, of *Dictyotaceæ*. Then as for the so-called tetraspores, they are extruded without a membrane, though they soon secrete one. But their condition on emission is, to say the least, just as consistent with loss of cilia as with loss of membrane; it is a physiological condition of which too much can readily be made. As for the number—four—which has suggested the comparison with the tetraspores of the *Florideæ*, even that is inconstant. The prevailing number is certainly four, but frequently only two, or rarely, one. No trichogyne or corresponding body has been observed, and the sorus of presumptive female reproductive bodies answers very much better for degenerate *Phæophyceæ* than for *Florideæ*. The presumptive oogonia are motionless, so are the corresponding bodies in *Tilopteridaceæ*, so are the oospheres of *Fucaceæ*. The character of the vegetative organs is overwhelmingly in favour of *Phæophyceæ*. The *Dictyotaceæ* in fact are most interesting when compared with *Cutleriaceæ*, in which all three kinds of reproductive bodies are ciliated. The growth of the thallus is certainly different, since in *Cutleria* it is trichothallic. But it may be recalled that the growth of the *Aglaozonia* or non-sexual forms of *Cutleria* is not trichothallic but by marginal initials. It would, moreover, be unwise to insist too much on this when we remember the tuft of hairs at the apical dimple in

very young *Fucus* plants, for example, which may indicate as other facts do, that there is no great gulf separating trichothallic growth from that by an apical cell, or group of equivalent initial cells.

These few facts not commonly brought together, and apt to be taken for insignificant in themselves, may nevertheless help us to think less of the differences that exist and cause confusion in the classification of the orders of *Phæophyceæ*, and more of the points, many of them more obvious than those I have cited, which lead us to group them altogether in one great sub-class.

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BUDDING IN TUNICATA.

NOTE.

CORRIGENDUM.—Upon referring again to Fol's memoir on the Appendiculariidæ (a work which I was unable to consult when writing my recent article on Budding in Tunicata), I find that two unessential details in that article require correction. Fol cannot be credited with the theory to which I referred on pp. 51 and 52, in spite of the ambiguity of his remarks on *Doliolum* (Fol, p. 6, footnote); and *Kowalevskia*, to which I referred on p. 52, seems in reality (Fol, pl. xi., fig. 5) to possess a circlet of fine cilia in its branchial canals, although no statement to this effect is made in the text, and no cilia are represented on pl. xi., fig. 5.

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